

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:	Michael Gavin Proctor et al.	Confirmation No.:	6206
Serial No.:	10/581,563	Group Art Unit:	1796
Filed:	June 2, 2006	Attorney Docket No.:	71049-012
Examiner:	Moore, Margaret G.		
For:	METHOD OF MAKING KAOLIN CONTAINING SILICONE RUBBER COMPOSITIONS		

**PETITION FOR ENTRY OF REQUESTED
EVIDENCE AFTER FILING OF APPEAL BRIEF**

Mail Stop PETITIONS

Attn: Office of Petitions

Director of the USPTO & Director of Patent Technology Center 1700

P.O. Box 1450

Alexandria, Virginia 22313-1450

Dear Sirs:

The Applicant hereby respectfully petitions the Directors of the USPTO and Technology Center 1700 to enter the attached evidence into the file wrapper of the above-referenced application pursuant to at least one of 37 CFR §§1.182, 1.183 and/or MPEP §§1002, 1002.02(c). The Applicant concurrently files a Reply Brief in conjunction with this Petition and the Petition Fee set forth in 37 CFR §1.17(f).

Brief Summary of File History and Reasoning for Submission of the Instant Petition:

The Applicant filed a Response and Declaration Under 37 CFR §1.132 on April 27, 2009. The Applicant subsequently filed a Notice of Appeal on September 29, 2009 and an Appeal Brief on November 30, 2009 referring back to the Declaration. In the Examiner's Answer to the Appeal Brief mailed on February 26, 2010 (and in an updated Answer mailed on March 29, 2010),

the Examiner concluded that she could not accept the factual statements of the Declarant set forth in the Declaration without reviewing additional evidence that corroborated and supported these statements. Said differently, the Examiner asserted that she could not accept the Declarant's statements on their own merit and required additional documentation that would confirm the knowledge and understanding of those of skill in the art.

Importantly, the first time during prosecution that the Examiner requested this additional evidence was in her Answer. Thus, the Applicant was clearly unaware of this request, and thus unable to submit this evidence, during prosecution or even concurrently with the Appeal Brief. As such, the Applicant hereby petitions the Directors to enter the supporting evidence, attached hereto as Exhibit A, into the file wrapper to ensure that the Examiner can properly review the evidence in conjunction with the Declaration and respond, if necessary.

Rule-Based Support For This Petition:

The Applicant fully realizes and appreciates that MPEP §1206 and 37 CFR §41.33 state that affidavits and *other evidence* submitted after the date of filing an appeal will not be permitted except under specific circumstances and that evidence received after jurisdiction has passed to the Board should not be considered by the Examiner unless the case is remanded by the Board. The Applicant also appreciates the USPTO's concerns with efficiency and the public policy that disfavors continual submission of evidence during an Appeal.

However, in the instant case, the Applicant respectfully petitions that the supporting evidence, attached hereto as Exhibit A, be entered into the file wrapper at the discretion of the Directors. In support of this Petition, the Applicant cites multiple sections of both the MPEP and the CFR below. The Applicant respectfully submits that all of these sections provide adequate and appropriate grounds for the Directors to grant this Petition and enter the attached evidence into the

file wrapper.

I. Jurisdiction of the Patent Application and Appeal Currently Remains With The Director of the Patent Technology Center

Pursuant to MPEP §§1002.02(c)(8) and 1206, the Applicant may file a petition with the Director of the Patent Technology Center concerning appealed patent applications before the transfer of jurisdiction to the Board of Patent Appeals and Interferences. As set forth in 37 CFR §41.35, jurisdiction over appeals typically passes to the Board upon transmittal of the file, including all briefs and examiner's answers, to the Board (e.g. after a Reply Brief is filed). (See also MPEP §1208)

In the instant case, the Applicant is filing this Petition concurrently with a Reply Brief. For this reason, the Applicant respectfully submits that jurisdiction of the patent application and appeal currently remains with the Director of the Patent Technology Center and petitions that the Director enter the attached evidence into the file wrapper.

II. 37 CFR §1.182 Allows for Petitions to the Director of the USPTO for All Questions Not Specifically Provided for in the Code of Federal Regulations

As set forth in 37 CFR §1.182 and recited in MPEP §1002, all situations not specifically provided for in the regulations will be decided in accordance with the merits of each situation by or under the authority of the Director of the USPTO. The Applicant recognizes that the instant situation is fairly unique and submits that the Examiner's request for additional evidence is necessary for the equitable and proper consideration of the Declaration, determination of patentability, and adjudication of the Appeal. As such, the Applicant hereby petitions the Director of the USPTO to enter the attached supporting evidence into the file wrapper.

III. 37 CFR §1.183 Allows for Suspension of the Rules in Extraordinary Situations

As set forth in 37 CFR §1.183 and MPEP §1002.02(b)(2), in an extraordinary situation, when justice requires, any requirement of the regulations in this part which is not a requirement of the statutes may be suspended or waived by the Director or the Director's designee on petition of the interested party. The Applicant appreciates that the instant situation is unique and submits that justice requires that the attached supporting evidence be entered into the record for the equitable and proper consideration of the Declaration, determination of patentability, and adjudication of the Appeal. The Applicant also respectfully submits that it would be inequitable to require the Applicant to spend additional funds to withdraw the Appeal, file an RCE to enter the evidence, and then potentially have to re-file the Notice of Appeal and Appeal Brief. Said differently, the Applicant submits that it would be inequitable to require that the Applicant restart the prosecution process. Accordingly, the Applicant hereby petitions the Director to enter the attached supporting evidence into the file wrapper.

The Applicant is submitting this Petition in conjunction with the Petition Fee set forth in 37 CFR §1.17(f). While it is believed that no further fees are presently due, the Commissioner is authorized to charge the Deposit Account No. 08-2789, in the name of Howard & Howard Attorneys PLLC for any fees or credit the account for any overpayment.

Respectfully submitted,

HOWARD & HOWARD ATTORNEYS PLLC

Date: April 26, 2010

/David M. LaPrairie/

David M. LaPrairie, Registration No. 46,295

Howard and Howard Attorneys PLLC

450 West Fourth Street

Royal Oak, Michigan 48067

(248) 723-0442

Appendix A:

Additional Evidence For Review by the Examiner

Reference 1: Chemistry and Technology of Silicones

W. Noll, *Chemistry and Technology of Silicones*, 400-401 (Academic Press, 1968)

Reference 2: Handbook of Elastomers

A.K. Bhowmick and H.L. Stevens, *Handbook of Elastomers*, 610 (2 ed., Marcel Dekker, Inc., 2001)

Reference 3: Silicone Elastomers/Rubber – Structure and Properties

Silicone Elastomers/Rubber – Structure and Properties, Dow Corning Corporation, <http://www.dowcorning.com/content/discover/discovertoolbox/forms-rubber-structure.aspx> (accessed 04/07/2010)

Reference 4: Elastomers, Plastics & Composites Fillers

Elastomers, Plastics & Composites Fillers, Wacker Chemie AG, <http://www.wacker.com/cms/en/products-markets/plastics/processingaids/fillers/fillers.jsp> (accessed 04/07/2010)

Reference 5: New Trends in Silicone Elastomer Technology

J. Amarasekera, *New Trends in Silicone Elastomer Technology*, Rubber World, 26-35, (June 1, 2000)

Reference 6: Comparing Liquid and High Consistency Silicone Rubber Elastomers: Which is Right for You?

B. E. Wolf, *Comparing Liquid and High Consistency Silicone Rubber Elastomers: Which is Right for You?*, Medical Plastics and Biomaterials Magazine, July 1997

Reference 7: Silicone Elastomers

P. Jerschow, *Silicone Elastomers*, 5 (Rapra Reports, Report 137, Vol. 12, No. 5, 2001)

Reference 8: Carbon Nanotubes: Exceptional Reinforcing Fillers for Silicone Rubbers

L. Bokobza and M. Rahmani, *Carbon Nanotubes: Exceptional Reinforcing Fillers for Silicone Rubbers*, Raw Materials and Applications, KGK März 112-117 (2009)

Chemistry and Technology of Silicones

by WALTER NOLL
Leverkuhn, Germany

With contributions to the chapters on technical applications by

OSKAR GLENZ, *Leverkuhn*; WILFRIED KNIEGE, *Leverkuhn*; WALTER
KRAUSS, *Leverkuhn*; HUBERT ROTHERT, *Berlin*; and BRUNO ZORN,
Leverkuhn

and to the medical part by

GERHARD HECHT, *Wuppertal-Elberfeld*

Translated from the second, revised and substantially expanded German
edition by B. HAZZARD, *Tooting, London*, and M. LANDAU, *Cheadle Hulme,
Cheshire, England* in collaboration with EXPRESS TRANSLATION SERVICE,
Wimbledon, London.

1968



ACADEMIC PRESS New York and London

Preface to the Second German Edition

The rapid development of the field of silicones has made it desirable to bring out a new, amended edition of this book; I am grateful to Verlag Chemie for making it possible to achieve this aim.

The whole work has been thoroughly revised and updated, as a result of which its size has been increased by almost fifty percent. More than half of the text has been rewritten. Particularly heavily revised and expanded are those sections of Chapters 8-10 that deal with the technology of silicone rubber; Chapter 4, which deals with the chemistry of the organofunctional silicon compounds; and Chapter 7, which gives an account of copolymers and condensates. The necessity of rewriting Chapters 4 and 7, in particular, shows clearly the direction of the most intensive work in silicone chemistry.

In spite of its expanded scope, the book retains the nature of a monograph giving the reader in condensed form not only a wide-ranging but also a thorough review of this rapidly growing field. In contrast to some other monographs on organosilicon compounds that have appeared in the interim, the silicones occupy in this as in the first edition the central position, and the technological part of the work is entirely devoted to them. In the chemical part it was necessary to broaden the range in order to provide the reader with a basis for understanding the present-day technological situation and with information that could be useful for further work. In view of the great volume of published literature, such an aim made it necessary to omit many detailed aspects of the field, increasing the danger of disagreement concerning the best selection of material.

As in the first edition, some contributions to the chapters on technical applications and on medical questions have been written by the author's

COPYRIGHT © 1968, BY ACADEMIC PRESS INC.

ALL RIGHTS RESERVED.

NO PART OF THIS BOOK MAY BE REPRODUCED IN ANY FORM,
BY PHOTOSTAT, MICROFILM, OR ANY OTHER MEANS, WITHOUT
WRITTEN PERMISSION FROM THE PUBLISHERS.

ACADEMIC PRESS INC.

111 Fifth Avenue, New York, New York 10003

United Kingdom Edition published by

ACADEMIC PRESS INC. (LONDON) LTD.

Buckley Square House, London W.1

First published in the German language under the title

"Chemie und Technologie der Silikone," copyright 1960

by Verlag Chemie GmbH, Weinheim/Bergstrasse, Germany

LIBRARY OF CONGRESS CATALOG CARD NUMBER: 67-22772

PRINTED IN THE UNITED STATES OF AMERICA

weight of silicone rubber gum, 20.0–200 parts by weight of fillers, 0.5–3.0 parts by weight of the curing agent, 0.0–5.0 parts by weight of pigments, and varying amounts of special additives.

The type of gum to be used in any particular case is selected from the materials described in Section 8.1.1, according to the properties required of the raw material or the vulcanizate. In many cases reclaimed silicone rubber can be used to replace part of the silicone rubber gum.

The properties of both the unvulcanized compounds and vulcanizates can be varied within wide limits as functions of the nature and amount of the fillers (36, 244). The mechanical properties of unfilled silicone rubber are unsatisfactory. As with other noncrystallizing types of synthetic rubbers, the addition of fillers, preferably reinforcing fillers, is necessary to obtain technically useful vulcanizates.

The highest reinforcing effect is obtained with *fumed silicas*, which have BET surface areas of 150 to 400 m²/gm. Unvulcanized silicone rubber compounds containing such fillers exclusively or predominantly are generally characterized by a relatively high Mooney viscosity and undergo a pronounced, but reversible, hardening during storage. The vulcanizates are characterized by high tensile strength. Fumed silicas impart only moderate hot-air stability to the vulcanizates; in so-called closed systems, on the other hand, these fillers are second only to products made hydrophobic with organosilanes.

Precipitated hydrated silicas are somewhat less reinforcing than the fumed silicas mentioned above and, in comparable amounts, therefore give compounds with a lower Mooney viscosity, lower green strength, and lower tendency to hardening during storage. The tensile strength of the vulcanizates containing such fillers is lower than for fumed silicas. The hot-air stability of the vulcanizates is substantially improved by precipitated silicas, while their stability in closed systems is definitely impaired. These fillers are also generally less suitable for the production of optimum dielectric properties and for articles of high transparency than the fumed silicas.

Fillers with a weak reinforcing effect (semi-reinforcing fillers) are, in particular, various specially treated *natural products*. Diatomaceous earths (diatomaceous mineral fillers) are the main products used. Because of their low reinforcing effect, it is possible to use large amounts of fillers while retaining good processing properties. As compared with the highly reinforcing fillers, these semi-reinforcing fillers give, at the same Shore hardness, a smaller increase in volume on swelling in oils and better compression set properties.

The examples of Table 70 show how the mechanical properties depend on the type and amount of filler added. All compounds contained a silicone rubber of type VS1; the figures given under "compounding formulation" are parts by weight.

(145). Industrially, Van de Graaff generators are generally preferred to a ⁶⁰Co source, since they provide an accurately focused and uniform radiation. In contrast, a ⁶⁰Co source gives a diffuse radiation whose energy of 60 to 140 W falls during its use in irradiation. No vulcanization auxiliaries of any kind and, in general, no elevated temperatures are necessary for the radiation cross-linking of silicone rubber.

As cryoscopic molecular-weight determinations on polydimethylsiloxanes irradiated with electrons have shown, 1.44 cross-linking sites appear per ion pair; 22 eV is necessary per cross-linking site (35). The average amount of radiation required for cross-linking is about 10 Mrp. However, the necessary dose may deviate considerably from this figure for other types of silicone rubber. In general, polymerizates not containing vinyl groups require a somewhat higher dose than those containing vinyl groups. The energy required also becomes considerably greater as the amount of phenyl groups is increased.

The properties of vulcanizates cross-linked by high-energy radiation scarcely differ in the unaged state, from products cross-linked with peroxides and with the same degree of cross-linking. It is better resistance to hydrolytic depolymerization on aging in humid atmospheres at elevated temperatures. The main reason for this is the absence of peroxide decomposition products which could act as depolymerization catalysts (243). However, it is possible that high-energy radiation gives a more stable type of cross-linkage (164).

If radiation vulcanization is carried out in the presence of polyvalent metal compounds or if halogen-containing polymers are added to the silicone rubber, the cross-linkage stability and the heat resistance of the products are improved still further (11).

Vulcanization by high-energy radiation is also affected by the nature of the filler, besides other factors. For example, compounds containing carbon black can be vulcanized more easily than those containing highly disperse silica (169).

8.1.3 MANUFACTURE OF VULCANIZED SILICONE RUBBER ARTICLES

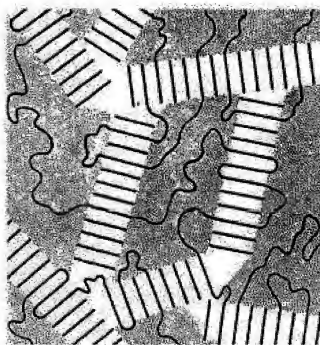
8.1.3.1 Heat-Vulcanizable Silicone Rubber

The processing of heat-vulcanizable silicone rubber corresponds fundamentally to normal rubber technology and is therefore generally performed by the rubber industry.

8.1.3.1.1 Formulation of compounds. Silicone rubber (gum) compounds have simple formulations as compared with those made up from organic elastomers. They consist essentially of *gum, fillers, and curing agents* (vulcanization auxiliaries). *Pigments* and special additives are used to achieve special effects. The basic formulation is somewhat as follows: 100 parts by

HANDBOOK OF ELASTOMERS

Second Edition, Revised and Expanded



edited by

Anil K. Bhowmick

Howard L. Stephens

ISBN: 0-8247-0383-9

This book is printed on acid-free paper.

Headquarters

Marcel Dekker, Inc.
270 Madison Avenue, New York, NY 10016
tel: 212-696-9000; fax: 212-685-4540

Eastern Hemisphere Distribution

Marcel Dekker AG
Hutgasse 4, Postfach 812, CH-4001 Basel, Switzerland
tel: 41-61-261-8482; fax: 41-61-261-8896

World Wide Web

<http://www.dekker.com>

The publisher offers discounts on this book when ordered in bulk quantities. For more information, write to Special Sales/Professional Marketing at the headquarters address above.

Copyright © 2001 by Marcel Dekker, Inc. All Rights Reserved.

Neither this book nor any part may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, microfilming, and recording, or by any information storage and retrieval system, without permission in writing from the publisher.

Current printing (last digit):

10 9 8 7 6 5 4 3 2 1

PRINTED IN THE UNITED STATES OF AMERICA

methyl groups, their initials precede the MQ (e.g., V indicates vinyl groups, P, phenyl groups, and F, 3,3,3-trifluoropropyl groups).

2.3 Reinforcement

It is necessary to reinforce the siloxane polymers used in elastomer applications. This is the case since the typical linear diorganosubstituted polysiloxanes used in commercial silicone elastomers are amorphous, flowable polymers at room temperature and have only approximately 0.34 MPa tensile strength when crosslinked. It is indeed fortunate that the strength can be increased by a factor as high as 40 (to the 13.8 MPa range) by the addition of special silica fillers. This is certainly phenomenal, since a comparative factor of only 10 is realized with amorphous organic rubber polymers such as SBR, NBR, and polybutadiene (Na polymer). Most commercially available silicone elastomers have tensile strength values ranging from 5.6 to about 10.5 MPa.

The exceptional increase in tensile strength of silicone polymer by silica compared to the more modest increases observed for amorphous organic rubber polymers is chiefly influenced by strong polymer-filler bonding and the sizable response of tensile strength increase with structure. This latter point is clearly demonstrated in Figure 5 by the work of Polmanter and Lentz (1975). The strong bonding of the silica filler to the polymer is related to the combination of chemical and physical bonds. The physical bonds are strong and include both van der Waals

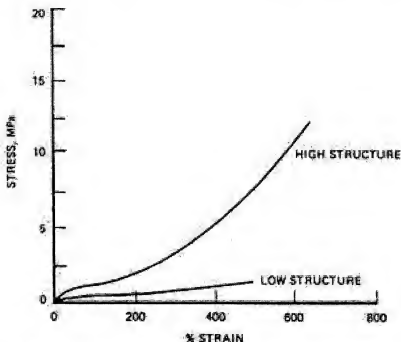


Fig. 5 Stress-strain curves to rupture for silicone elastomers filled with low- and high-structure silica. The ultimate particle size for both silicas was 5.8 nm, and the pore volumes were 0.6 and 5.8 cm^3/kg . (From Polmanter, 1981.)

Reference 3



*We help you
invent the future.™*

Log In | Profile/Preferences | Customer Support | Contact Us | Global (English) | Change

Search Products



Products Technical Library Solutions Premier Services About Dow Corning

Home > Discovery Center > Toolbox

Discovery Center Home

[B Silicone Showcase](#)
[B Toolbox](#)
[B Forms](#)
[B Safety & Sustainability](#)
[Proven Innovation](#)
[Chemistry Corner](#)

Fascinating Silicone™ The Versatile Silicone Toolbox Elastomers

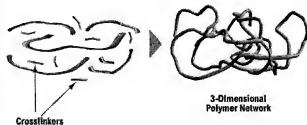


Silicone elastomers/rubber - structure and properties

Structure

Silicone polymer + filler + crosslinker (vulcanizing agent) = silicone elastomer

Silicone elastomers are crosslinked linear silicone fluids or gums with a three-dimensional structure.



Silicone elastomers contain fillers:

- Reinforcing fillers, like silica, which interact with the base polymer and increase the strength of the elastomer
- Extending fillers, like quartz, distomers, or metal oxides, which help reduce the material's cost

They also contain a crosslinker (vulcanizing agent).

Silicone elastomers differ from linear silicone fluids in three ways

Linear Polymers	Elastomers
Physical properties determined by chain length	Physical properties determined by degree of crosslinking
Linear polymers are liquids; viscosity increases with molecular weight	Elastomers are solids with indefinite molecular weight
Soluble in solvents	Swell in solvents

Properties

- Excellent high/low temperature performance capability (standard grades of silicone elastomers can handle temperatures ranging from -40 to 200 °C/-40 to 392 °F)
- Very flexible – flexibility virtually unaffected by temperature
- Excellent ozone resistance
- Excellent UV resistance
- Excellent electrical insulating properties
- High thermal conductivity
- Excellent resistance to a wide range of fluids and chemicals
- Excellent weatherability
- High gas and drug permeability
- Easy to fabricate/process

Did You Know ... the source of silicone's exceptional high and low temperature performance capabilities is its low viscosity/temperature coefficient!

Did you know ... there are six different ways silicone materials can be cured!

Get answers

Have a question about silicone?

Ask an Expert



Expand your understanding

Just for fun: What is the difference between an elastomer and a rubber?

Read: Some Like It Hot (PDF size 259 KB) - why silicones perform better than other elastomers in extreme temperatures.

Imagine your next design with silicones: Tour the Dow Corning Industrial Design Studio.

Learn about silicone elastomers from Dow Corning: Explore products for your application.

Stay informed

Sign up for free e-mail updates about silicone materials and technologies from Dow Corning.

Enter e-mail address

Subscribe

Privacy Statement

< back to Toolbox Home Page

[Media Center](#) | [Careers](#) | [Site Map](#) | [Other Dow Corning Websites](#)

Using this website means you understand our [Privacy Statement](#) and agree to our [Terms & Conditions](#).

©2000 - 2010 Dow Corning Corporation. All rights reserved. Dow Corning is a registered trademark of Dow Corning Corporation. XJAMETER is a registered trademark of Dow Corning Corporation. We help you invent the future is a trademark of Dow Corning Corporation.

www.wacker.com

ELASTOMERS, PLASTICS & COMPOSITES FILLERS

HDK® as a Reinforcing Filler

The reinforcing filler HDK® imparts the requisite mechanical properties to natural and synthetic rubbers and silicone elastomers. Hydrophobic HDK® grades can be used to produce combinations of high filler loading or tear strength with good processability.

Tailored Elasticity

For optimum results, the fillers used in natural and synthetic rubber and silicone elastomers must meet specifications. That is the only way to achieve products with precisely defined mechanical properties, such as tensile strength, elongation at break and tear strength (notch impact strength/Shore hardness). The reinforcing filler HDK® is a preferred auxiliary for achieving the desired system property.

Optimum Reinforcement

HDK® owes its outstanding reinforcing effect to its high specific surface area. The numerous interactions between the polymer chains of the elastomer network and the special particle structure of HDK® dissipates mechanical stresses and forces within the elastomer network – and so restricts the entropy space for polymer chains. This process increases the elastomers' strength, elongation at break and load-bearing capacity.

High Sag Resistance

HDK® may be added to nonpolar silicone rubber to act both as reinforcing filler and rheological additive. The marked thickening action of hydrophilic HDK® provides the requisite degree of sag resistance, with the result that low-viscosity systems do not run down vertical surfaces.

Good Processability

In silicone elastomers, hydrophilic HDK® provides a high reinforcing effect – but at the same time results in a high viscosity, thereby limiting processability. One solution here is to use processing auxiliaries and low-molecular plasticizers. They block the interaction between the HDK® particles by adsorption and thus lower the viscosity. The system benefits from smooth running and perfect processing.

Your selection resulted in 9 product recommendations.

Products	Application	Product Group	Product Type	Effect	BET surface
HDK® H15	Reinforcement of mechanical properties	Pyrogenic Silica	Hydrophobic	Reinforcement	130 - 170 m2/g
HDK® H20	Reinforcement of mechanical properties	Pyrogenic Silica	Hydrophobic	Reinforcement	170 - 230 m2/g
HDK®	Reinforcement of mechanical	Pyrogenic	Hydrophobic	Reinforcement	170 - 230

H2000	properties	Silica			m2/g
HDK® H30	Reinforcement of mechanical properties	Pyrogenic Silica	Hydrophobic	Reinforcement	270 - 330 m2/g
HDK® N20	Reinforcement of mechanical properties	Pyrogenic Silica	Hydrophilic	Reinforcement	170 - 230 m2/g
HDK® T30	Reinforcement of mechanical properties	Pyrogenic Silica	Hydrophilic	Reinforcement	270 - 330 m2/g
HDK® T40	Reinforcement of mechanical properties	Pyrogenic Silica	Hydrophilic	Reinforcement	360 - 440 m2/g
HDK® V15	Reinforcement of mechanical properties	Pyrogenic Silica	Hydrophilic	Reinforcement	130 - 170 m2/g
HDK® V15P	Reinforcement of mechanical properties	Pyrogenic Silica	Hydrophilic	Reinforcement	130 - 170 m2/g

New trends in silicone elastomer technology

by Frank S. Burkus II and Jay Amarasekera, General Electric Silicones

Silicones have been interesting materials since Kipping developed a convenient method of producing organosilanes in 1904 (ref. 1). Silicones, or polyorganosiloxanes, possess a variety of material features not available in any other singular polymer family, due to their flexible, inert backbone consisting of alternating silicon and oxygen atoms. Table 1 lists the physical and chemical properties of various polymer systems.

The free rotation of the silicon and oxygen atoms results in an extremely high degree of flexibility under harsh environmental conditions. The Si-O bond (at 369.3 KJ/mol) is stronger than a typical C-C bond (347.9 KJ/mol), and longer (1.64 Angstroms vs. 1.53 Å) (ref. 2). This combination of strength and flexibility make siloxane polymers a natural choice for sealing, dampening, deflecting or wherever an elastomeric material is required.

By varying the substituents on the silicon atom, as table 2 indicates, the properties of the resulting polymer can be influenced significantly.

Depending on the properties desired, a siloxane material could be designed by using polymers containing any of the above substituents attached. An example of this would be the use of fluoro-substituted siloxane polymers in applications, which must withstand exposure to solvents and corrosive oils. If extreme low temperature resistance were needed, the siloxane material would have some phenyl substituted siloxane polymers in place of or in addition to polydimethyl or polymethyl vinyl siloxane.

Silicone elastomers

When linear versions of the above polymers are compounded with a reinforcing filler (typically fumed silica), a special type of siloxane known as an elastomer is formed. Silicone elastomers are flexible materials possessing a large amount of internal physical strength when compared to other siloxane products such as pressure sensitive adhesives, resins or other systems. Table 3 illustrates the variety in the product line.

Siloxane elastomers can be classified into three distinct categories based on processing: pourable, pumpable and millable. The end application will determine the type of elastomer needed by taking into account the material requirements and the processing parameters. Only by coupling the correct processing with the correct material properties will a useful elastomeric system be obtained.

Pourable elastomers are made with low molecular weight siloxane polymers (10,000-100,000 g/mol), low amounts of reinforcing filler <15 parts, and additional additives. Since the polymer molecular weights are that of a fluid and the loading of the filler is modest, it is necessary to add cross-

Table 2 - substituent effects on siloxanes

Substituent group	Imparted quality
CH ₃ (methyl)	General purpose
C ₆ H ₅ (phenyl)	Extreme low and high temperature resistance
CH = CH ₂ (vinyl)	Network control, high durometer, strength
CH ₂ -CH ₂ -CF ₃ (fluoro)	Fuel and solvent resistance

Table 1 - properties of various rubbers

Property	Silicone	PTFE	SBR rubber	Butyl rubber	Oil based rubber	PVC	Polyethylene
Temp., (°C) rating	-40 to 200	250	75	90	75	60 to 105	75
Mech. water absorption mg/cm ²	1.6	0.8	2.3	1.2	3.9	1.4	0.08
Resistance M ohm	30,000	50,000	2,000	30,000	21,000	2,000	50,000
Tensile, MPa	8.27	13.79	5.52	5.52	8.27	10.34	10.34
Elongation, %	>400	150	350	400	300	200	400
Heat age 5 days @ 200°C	Excellent	Excellent	Fails	Fails	Fails	Fails	Melts
Cold bend @ 55°C	Pass	Pass	Fail	Pass	Fail	Fail	Pass
Ozone resistance	Excellent	Good	Poor	Good	Good	Very good	Good
Chemical resistance	Good	Excellent	Fair	Fair	Poor	Very good	Very Good
Processing	Good	Poor	Good	Good	Good	Very good	Very good

Table 3 - various siloxane products

Siloxane type	Duro.	Tensile (Mpa)	Elongation	Density
Heat cured rubber	45	4.8-7.4	100-400	1.180
Resin/glass laminate	n.a.	200-240	2	890
One part silicone sealant	26	2-93	540	1.007

linkers and other functional species to increase the physical strength of these materials. These elastomers are cured via either a condensation or addition reaction, depending on the formulation and catalyst system used. The pourable elastomers are usually sold as two part systems in a variety of ratios. In any case, the mixtures of starting components are such that the pre-cured material has a viscosity in the range of 100-1,000,000 mm²/s @ 25°C, which is pourable (ref. 3). Pourable siloxane elastomers are typically applied as a mold in place material, or poured into a mold using low pressures. Once mixed and prior to molding, the materials need to be de-aired to remove any entrapped gases from mixing.

Independent of the mechanism, these materials are cured thermally at moderate temperatures. RTVs, or room temperature-vulcanized rubbers, undergo curing at room temperature.

Millable elastomers are composed of very high molecular weight organosiloxanes and large amounts of reinforcing filler (300,000-800,000 g/mol, and >20 parts of filler, respectively). The polymers used in this type of elastomer are linear in nature, and the crosslinking is typically accomplished through functional organic groups attached to the silicon atoms on the polymer backbone. Catalysts in these products are either peroxides or transition metals, depending on the formulation and end use of the product. The compounds are processed via mixing the uncatalyzed rubber with the catalyst of choice, followed by subsequent compression molding or injection molding. Due to the high green strength of the gum-based system, extrusion is also a possible manufacturing process.

An alternative to millable and pourable systems is the pumpable siloxanes, commonly called liquid silicone rubbers. Liquid injection molding silicone elastomers were developed at General Electric Silicones in 1975 to fill the need for an easily processable alternative to millable, high consistency rubber (ref. 4). Liquid injection molded silicone elastomers are made from moderate viscosity siloxane polymers compounded with reinforcing filler, crosslinker and a curing catalyst. The curing system of choice in a liquid injection molding process is based on platinum catalyzed hydrosilylation (ref. 5). This type of catalysts has several inherent benefits including very quick cycle times, thick and thin section cure and no reaction by-products.

High productivity is the hallmark of a liquid injection molding system, and short cycle times are critical to a productive system. Typical cycle times for a liquid injection molded elastomer system are on the order of tens of seconds, as opposed to minutes for many other elastomer systems. The cure rate is determined by recording the torque as a function of time on a modulating disk rheometer. Typical torque/time curves are taken at 120°C and 177°C, and are shown in figure 1.

The T02 is time to 2% cure and this represents the injection

window of the material. In analogous fashion, the T90 is the time to 90% of the total curing of the material, and this represents complete cure of the sample. The max torque is a measure of the hardness of the material, and the peak rate tells how fast the curing is completed, once the process begins. The addition cure reaction is utilized in a liquid injection molding system due to the ability of the elastomer to simultaneously undergo both thick and thin section curing. Whereas a condensation process must remove the by-product to drive the reaction to completion, there is no small molecule evolution in an addition cure reaction. Therefore, as long as sufficient thermal energy is transferred to the bulk of the material, it will cure as quickly as the surface. This enables consistent curing in a part with unequal wall thickness.

The addition reaction is similar to metal catalyzed condensation in that the catalyst species stays present in the material after the curing has taken place. This differs with a radical or peroxide catalyzed system where the catalyst is destroyed during the molding process. In the condensation process, however, the remaining catalyst can take H₂O from the atmosphere and re-equilibrate the cured polymer network. This process is known as reversion and can affect the functional life of the elastomer. The platinum remaining in an addition cure matrix does not catalyze the reversion, because there are no unsaturated groups with which to associate, and therefore no active site can be generated (ref. 6). Figure 2 illustrates platinum-vinyl interaction and the subsequent reaction to form an ethane linkage.

The generation of the active site via a platinum/unsaturated carbon interaction is critical to the mechanism of hydrosilylation (ref. 6).

When compared to a millable silicone rubber, a liquid injection molded silicone elastomer has some inherent benefits which lead to increased productivity and lower the per part cost. The benefits of a liquid injection molded silicone elastomer system are illustrated in table 4.

Depending on the part to be molded, the number of parts and the capital required, a liquid injection molded silicone elastomer system may be economically favorable. It is recommended that a detailed cost analysis be performed on the

Figure 1 - modulating disk rheometer curve

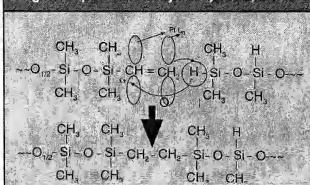
Cure rate evaluation



Mettler MDH2000E

	120°C	177°C
T02 (sec.)	29	6
T90 (sec.)	47	11
Peak rate (N·m/min.)	13.56	14.57
Max. torque (N·m)	16	15

Figure 2 - platinum catalyzed hydrosilylation



proposed process first using a liquid type system, then comparing it to a millable rubber system. Table 5 outlines a method for determining the true cost of a part. Although it is not as detailed as an actual analysis, it does illustrate the necessity of considering all of the costs in a processing system, and not just that of the material.

Experimental

The liquid injection molded silicone elastomer samples were press cured at 177°C for 15 minutes and cooled to room temperature prior to testing the tensile, elongation, tear, durometer and modulus. Tensile strength, die-B tear strength, % elongation and 100% modulus were tested on a Monsanto Tensometer 10, at a rate of 50.8 cm/minute until failure. The durometer was measured on an Exacta-Hardness Tester by NewAge using a Shore A stylus on press cured sheets. The application rate is a measure of the flowability of the material and was determined by extruding the material through a 3.17 mm orifice at 0.62 MPa and recording the amount in grams per minute. The cure rate of the materials was measured using a Monsanto MDR 2000E at 177°C. The compression set was measured by compressing 1.27 mm plugs of material, which were cured for 30 minutes at 177°C, to 75% of their original height in an air circulating oven at 177°C for 22 hours. The samples were allowed to cool at ambient conditions prior to recording the final set. Adhesion tests were per-

formed on lap shear specimens of the desired substrate using a 1.27 cm x 1.27 cm overlap with a 3.17 mm thick section of liquid injection molded silicone elastomer as an adhesive. The samples were cured in an air circulating oven for 30 minutes at 150°C, and allowed to cool to room temperature prior to testing to failure on the tensometer.

Results and discussions

Standard LIM materials

Liquid injection molded silicone elastomers were developed as a processing alternative to millable and pourable siloxane elastomers. Since the time liquid injection molded silicone elastomers were invented in 1975, the materials have become stronger, easier to produce, and have been developed to achieve unique properties dependent on the target application. It is possible to trace the industrial acceptance in liquid injection molded silicone elastomers by looking at the material improvements made over the past 24 years. Liquid injection molded silicone was originally used for small parts under moderate conditions. Examples of such include o-rings, small grommets, small gaskets, etc. The first liquid injection molded silicone elastomers were opaque, addition cure materials with high tear strength when compared to standard RTV (pourable) systems. They had inherent solvent and abrasion resistance and were cured via an addition cure process in less than two minutes at 177°C.

The performance characteristics of the initial liquid injection

Table 5 - cost analysis

Liquid injection molded silicones cost analysis		
	Liquid injection molded	HCE
Part 1		
Cycle time(s)	30	330
Cycles/day	2,640	238
Yield (%)	98	95
Number of cavities	24	40
Materials		
Price/pound (\$)	4.85	2.50
Mass/part(g)	10	10
Total material cost (\$)	108.975	57.987
Labor		
Cost/hour(\$)	20	20
Hours/day	22	22
Total labor cost	7,088	48,733
Secondary operations		
Inspection cost (\$)	5,000	21,000
Deflashing cost (\$)	0	31,000
Total secondary ops. (\$)	5,000	50,000
Part 2		
Total material cost (\$)	108.975	57.987
Total labor cost (\$)	7,088	48,733
Total secondary ops. cost (\$)	5,000	50,000
Total production costs (\$)	121,061	156,720
Total equipment usage (days)	16.1	110.8
Number of machines needed for job completion in 16.1 days	1	7
Liquid injection molded silicones vs. HCE cost analysis 1,000,000 parts		

Table 4 - liquid injection molded vs. heat cured silicone elastomers

Heat cured silicones	Liquid injection molded silicones
One component	Two component
Many processing steps	One processing step
• milling	No secondary operations
• preforming	• no post-baking
• molding	• no deflashing
• trimming	• no catalyst quenching
High molding pressures (34-47-137.89 Mpa)	Molding pressures (10-34-34.47 Mpa)
Long cycle times (>120s)	Short cycle times (10-40s)
Labor intensive process	Automated process
	• consistent pumping
	• consistent cure
	• one to one A/B mix
	• automatic mixing (static mixer)
	• computer-controlled cycle
	• automatic de-molding

tion molded silicone material were sufficient enough to gain acceptance after their introduction, and the material is still in use today. There were, however, some drawbacks with this material. It was not clear, had a rather high specific gravity, and the cure rate of the material was almost two minutes. This cure cycle is too long to take full advantage of the productivity, which a liquid injection molding system has to offer.

The next improvement in liquid silicone elastomer chemistry was the introduction of a clear, fast curing product line. The material had the physical strength of the original liquid injection molded elastomer series, but was optically clear, had a low specific gravity, and cured in <30 seconds at 177°C.

This series has found uses in applications ranging from medical to electronics to consumer goods, and represents the liquid injection molded silicone elastomers with the highest physical strengths, the fastest cure rates and the lowest specific gravity. There are some applications which this line does not fill, including areas where low compression set is needed, where self-bonding is required or where the end use requires the siloxane to have a controlled force deflection.

New developments in LIM material performance

Controlled force deflection, primerless adhesion and low

Table 6 - results of adhesion tests on various substrates with self-bonding liquid injection molded elastomer

Substrate	Adhesion
ABS	Good
Aluminum	Excellent
PBT	Excellent
Nylonamide (unfilled)	Good to excellent
Polycarbonate (unfilled)	Poor
Polycarbonate (UV treated)	Excellent
Polylithalamide	Excellent
Polypropylene	Poor
PTC/nylon	Excellent
PP/OPS	Good
PVC	Excellent
Steel	Excellent

compression set as molded are three key technology features which the new generation of liquid injection molded silicone elastomers must have. Advances have been made in all of the above areas, and the resulting new materials can be used in applications where previous liquid silicone rubbers performed insufficiently.

Controlled force deflection

The need for an elastomer that exhibits controlled deflection has been identified. This property is useful in medical systems where the elastomer is used as a spring in a pumping system, or in the electronics industry where a keypad requires a controlled force to work effectively. A series of liquid injection molded silicone elastomers having a controlled force deflection has been developed offering a wide range of physical properties and processing alternatives.

All of these materials have an extremely high application rate, which means that they can fill complex geometries, such as those used for pumps or keypads, and cure in a very short cycle time. The material selection will depend on the degree of physical strength required, and the longevity of the part. Figure 3 illustrates the force deflection characteristics, and the life cycle of two of these materials.

The controlled force deflection series of materials offers various physical strengths, application rates and degrees of longevity, thereby offering the design engineer a large degree of flexibility in platform materials, while maintaining a consistent deflection force.

Self-bonding

As a general rule, and partially by design, liquid injection molded silicone elastomers typically do not bond to substrates without priming and/or post-baking. LIM silicone elastomers are addition cure materials, and therefore do not have a large number of polar species at the surface of the material with which to interact with other materials. This type of non-functional surface is excellent for release properties, hence the reason why silicones are often used as release liners.

One reason siloxanes are so difficult to adhere to is that the surface energy of the cured siloxane is very low ~18 mN/m. The low surface energy prohibits other materials from wetting the surface of the siloxane. Wetting the surface means that the material must spread out in such a way that

Figure 3 - force deflection curve

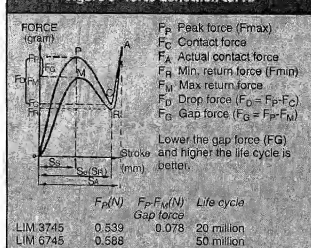
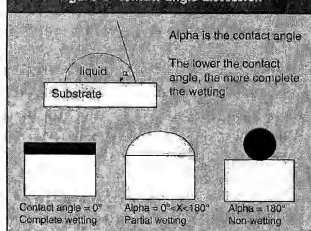


Figure 4 - contact angle discussion



the two surface areas become contacted in an intimate fashion. A material with a lower surface energy will wet a material with a higher surface energy. This is because the intramolecular interactions of the lower surface energy material are low enough to be overcome by the higher energy, substrate surface.

To determine the wettability of a material, contact angle measurements are typically used. A drop of a material is placed on a surface of known energy, and the angle between a tangent to the drop and the surface is measured.

As figure 4 shows, if the sample does not wet at all, the angle is 180°; if the sample completely wets, the angle is 0°. Various degrees of non-wetting and wetting occur between the two extremes. Silicones usually have very high contact angles, corresponding to very low surface energies, and therefore are difficult to wet. A drop of water on a silicone wax is a visual example of a non-wetting interaction.

Recently, there have been developments that have enabled the formulation of siloxanes that bond readily to engineering thermoplastics, glass and metals. The ability of self-bonding or primerless adhesion, enables a design engineer to take full advantage of the productivity of a liquid injection molded elastomer system by eliminating the priming step of the process. Additionally, a self-bonding elastomer enables certain design flexibility in the part itself, as the need to mechanically lock the elastomer in place no longer exists. The first generation self-bonding liquid injection molded silicone elastomers are translucent, have good physical properties and mold in less than 30 seconds at 177°C.

In addition to the fast cure and impressive physical profiles, the material has a low specific gravity, and a high application rate. The adhesive properties of this material were tested on many engineering thermoplastics and metals. The results of this test are given in table 6.

The values given in the table represent general materials categories, are qualitative, and do not represent absolutes. This is because the surface of the substrates can be affected by processing and contamination. Adhesion is purely a surface phenomenon, and therefore adhesion can be compromised by contamination, and impurities. Table 7 lists the results of a quantitative experiment on a single lot of 30% glass filled PBT.

The adhesive bond obtained through the use of this material is significant immediately out of the mold, and increases with time as the part stands at room temperature and pressure. To prevent the buildup of siloxane on the mold surface, the authors recommend that the mold undergo a semi-permanent Ni/PtFE coating prior to use. This enables easy removal of the part from the mold, and reduces the effort needed to perform routine cleaning on the mold.

Low compression set

In a typical addition cured siloxane elastomer, less than 100% of the functional groups are reacted. This is partially by design, as well as being a result of the vinyl and hydride being locked in the polymer matrix in positions which are not

Table 7 - Quantitative adhesion test data with self-bonding 8040

Substrate	Treatment	Siloxane type	Grade	Adhesion force	Failure mode
Aluminum	None	Non-bonding	LIM 8050	<0.69 MPa	100% adhesive
Aluminum	Primer	Non-bonding	LIM 6050	>1.72 MPa	100% cohesive
Aluminum	None	Bonding	LIM 8040	2.42 MPa	100% cohesive
PBT*	None	Non-bonding	LIM 6050	<0.69 MPa	100% adhesive
PBT*	None	Bonding	LIM 8040	2.38 MPa	100% cohesive

* 30% glass filled

in close proximity to one another. This is sufficient for the material to perform as designed at standard temperatures and pressures. However, if the material is exposed to extreme pressure and temperature for extended periods of time, the unreacted functional groups present within the cured siloxane network can react such that the part takes on a new set of dimensions. This phenomenon is called compression set, and the susceptibility of liquid injection molded silicone elastomers has limited their use in applications in high temperature, high stress environments.

There are methods of reducing the compression set properties of a liquid silicone elastomer such that it is suitable for use in gaskets and seals for under the hood automotive applications, and environments where low compression set is needed. The first of these methods is a post bake to drive the possible reactions to completion. In this technique, the part is cooked in an oven for several hours at temperatures near 200°C to drive the reaction of any remaining functional groups to completion. By post-baking one type of LIM, the compression set is reduced from a value of 45% to <20%. An alternative method is to fill the liquid silicone rubber with precipitated silica filler. This results in a system with good, as molded, compression set values typically in the teens.

There are drawbacks to each method, which must be emphasized. In post-baking a part, the entire cycle time of subsystem manufacturing is lengthened by the amount of the post-bake. This severely detracts from the profitability of a liquid silicone system. When compared to a heat cured elastomer, liquid silicones are profitable when you can have fast molding cycles. If you are post-baking a part for four hours, the actual molding cycle is not the rate limiting step, therefore reducing the cycle time does not save a large percentage of the total production time. As far as the precipitated system is concerned, the high filler loading results in a low tear system, and a very high specific gravity.

A new method of achieving a low compression set in liquid injection molded silicone elastomer systems has been recently developed in which a standard liquid injection molded silicone elastomer system is combined with an additive package to yield a low compression set product. The resulting liquid injection molded silicone elastomer has excellent physical properties, a fast cure cycle, low specific gravity and an as molded compression set of <20%.

This approach of creating a low compression set liquid injection molded silicone elastomer system has several advantages when compared to the aforementioned precipitated silica method. The specific gravity of the low CS liquid injection molded silicone elastomer is lower than the precipitated silica version. This results in a lower price per part, as parts are filled by volume (L) and the material is sold by

weight (g). Figure 5 compares the specific gravity of various liquid elastomers.

The tear strength of the material also suffers under the precipitated system, as figure 6 indicates. Even where tear strength is not a critical component of the part design, it is useful in part removal, and high tear strength will result in fewer parts which need to be scrapped due to tears during processing.

Ultimate material benefits are obtained when the low compression set properties are combined with the self-bonding attributes to yield a liquid injection molded elastomer that has both. This material is perfectly suited for under-the-hood automotive applications.

LIM processing

The term liquid injection molded silicone elastomers refers to the method by which the siloxane is processed, via injection molding. When the overall process map of this method of producing siloxanes (thermosets) is compared to that of other injection molded elastomers and thermoplastics, many similarities can be seen.

The LIM material is pumped in a 1:1 ratio into a static

Table 8 - liquid injection molded silicone/ETP process comparison

Typical processing conditions:	Silicone (LIM)	Thermoplastic material
Material type	Thermoset	Thermoplastic
Typical mold temperatures (°C)	149-204	267-107.2
Typical material processing Temperatures (°C)	267-37.4	204-399
Typical injection pressures (MPa)	6.89-34.47	68.94-137.89
Typical cycle (sec.)	30-60	10-40
Cure time (sec.)	25-55	8-35

mixer and fed into the barrel of the injection molding machine. The material is then fed into the injection nozzle by either a screw or a ram type unit, depending on the style of the machine. The screw is the most common method of transfer due to the similarity to thermoplastic molding, while the ram/plunger method is gaining in popularity due to the high accuracy and repeatability of each shot of material. Until this point, the material is maintained near room temperature to minimize the amount of pre-curing that takes place. This precaution must be taken because once the catalyst is present with the crosslinker (i.e., after the A and B are mixed in the static mixer) the material can cure at elevated temperatures. The material is injected through a chilled nozzle, into a heated mold. The molding takes place for anywhere from 10-40 seconds and then the mold opens and the part can be removed. The mold can be either side or parting line gated, and the runners can either be chilled (cold) or heated (hot). A cold runner system saves material, but the tooling cost is usually higher, while a hot runner mold is a less expensive capital investment, but the entire runner will have to be scrapped because liquid injection molded silicone elastomers are thermosets and cannot be reused. A comparison of the molding conditions between liquid injection molded silicone elastomers and thermoplastics is shown in table 8.

Liquid injection molded silicone elastomers are often used to make discrete parts such as baby bottle nipples, floppy gaskets, washers, septa, o-rings, etc. There are some applications, however, which require a more advanced form of molding in which the elastomers are molded over a thermoplastic or metal carrier. This is known as overmolding and eliminates the need to mold a discrete gasket and assemble it with the carrier of choice, thereby generating productivity and a lower overall cost per part.

When overmolding, several considerations must be taken into account, including the plastic used, the cycle time of the process, the injection pressures, the siloxane material used and the molding design. The molding conditions must be conducive to the engineering thermoplastic (ETP) substrate over which you are molding in that Tg, Tm of the material must be compatible with the mold temperature, and the injection pressures must not deform the part during the molding cycle. It is recommended that the parts be preheated prior to overmolding such that the substrate does not act as a heat sink and slow the curing process to an undesirable cycle time.

Two-shot or two component molding

Ultimate efficiency and design flexibility are made possible

Figure 5 - durometer vs. density for various liquid systems

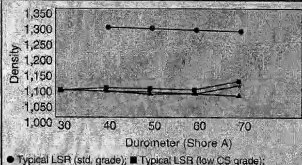
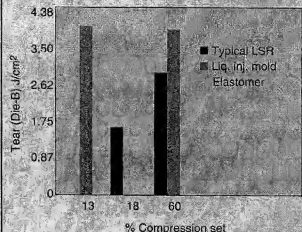


Figure 6 - tear vs. % compression set for various liquid systems



through the use of two component or two-shot molding, in which an ETP part is molded and a liquid injection molded silicone elastomer is molded over the plastic part in a single process. To achieve the goal of molding a thermoset and a thermoplastic in one process, it was necessary to break the overall procedure into three separate steps:

- The injection molding of the ETP initiates the whole process and is the fastest step, usually taking <20 seconds.
- While the material is still hot, the mold opens and the part is transferred to the liquid injection molded silicone elastomer tool in step two.
- Then the liquid injection molded silicone elastomer is molded on top of the ETP to complete the cycle. The mold opens, a completed part is removed, and the entire process starts over.

The key to the entire process is the transfer of the ETP part to the silicone molding section, and there are three methods whereby this can be achieved: Rotary plate, retractable core and rotary platen.

Rotary plate

Perhaps the most versatile method of two component molding utilizes a rotating plate to transfer the ETP to the liquid injection molding section. In a rotating plate design, the thermoplastic is injected into the thermoplastic mold and is cooled in the mold to a certain degree. Once the structural integrity of the part has been sufficiently achieved, the mold opens and the part is removed from both sides of the mold. The part is held by a center plate, which is rotated such that the plastic part is now positioned in between the two heated halves of the liquid injection molded silicone elastomer mold. The mold closes, and the silicone is molded atop the plastic part, while a new plastic part is being molded in the previous cavity at the same time. Once the elastomer molding cycle is complete, the mold opens again, separates from both sides of the part, the part is removed, the center plate rotates, the mold closes and the whole molding process is repeated. A schematic of this type of design is shown in Figure 7.

By having a complete and dedicated liquid injection molding side in addition to a complete thermoplastic side of the mold, it is possible to mold the elastomer onto both sides of the part. This ability offers significant design flexibility, however it also poses some technical challenges. The part must demold and remold on both sides in the middle of the molding process, which means that the tolerancing of the thermoplastic mold must be extremely tight for the part to consistently match the tolerancing in the liquid injection molded silicone mold.

Sliding core mold

Another way of molding liquid silicone elastomers onto thermoplastics is via a sliding core mold. Instead of demolding the part and moving it to a new location, the mold has the ability to form additional cavitation for the liquid silicone by an internal sliding mechanism. The ETP is molded in the first portion of the process, then as it cools, the mold changes shape to create a void for the silicone to fill. The silicone cavity can be formed via sliding pins or cores, and once this occurs, the liquid injection molded silicone elas-

tomers is molded in place.

Although this eliminates the need to rotate a mold, the mold design becomes very complex, depending on the type and amount of cavities needed. Another drawback is that the two processes, thermoplastic molding and liquid silicone molding, must be carried out in series. This results in two separate molding activities that must take place sequentially during the molding cycle, thereby reducing the overall productivity of the process.

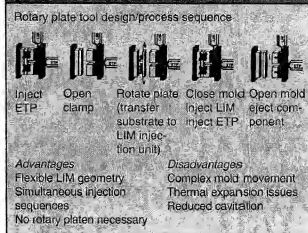
Rotating platen

The third mold design option available in a two component molding system is the rotating platen. In this design, three of the four mold cavities are of thermoplastic molding design, in that they are cooled to the temperature needed to mold the ETP portion of the part. Once the thermoplastic molding cycle is complete, mold opens and the part remains in half of the mold, then the entire half of the mold rotates to align the plastic part with the heated half of the liquid injection molded silicone elastomer. The mold closes for the liquid silicone molding, and at the same time another thermoplastic part is being molded. The liquid silicone mold uses the virgin thermoplastic as a shut off, and the entire thermoplastic cycle is completed while the LIM silicone elastomer is being molded.

The gain in cycle time comes at the cost of mold complexity. To take advantage of this method of two component molding, it is necessary to have the ability of sequential injections and gating. This, as well as the necessity of the entire mold to rotate, results in a more complex mold design. The rotating platen mold does not permit the molding of the liquid silicone elastomer onto both sides of the thermoplastic part, but only on the side which faces the heated silicone mold.

Independent of which type of mold system is utilized, there are other considerations which need to be taken into account when designing a two shot system. The gating type, either cold runner or hot runner, must be decided upon based on the mold complexity versus possible material loss. The process should have the flexibility of sequential gating. The location and size of vents must be identified. Even the

Figure 7 • rotary plate process map for two component molding



geometry of the ETP part is of concern to the liquid injection molding puzzle, as it can be used as a shut-off, and its latent heat can be used to help thermally cure the liquid injection molded silicone rubber.

The proper material must be chosen based on the part design. As a rule, the physical properties remain constant across the entire liquid injection molded siloxane product lines. Typical values are: Tensile strength 6.2-8.96 MPa; elongation 300-700%; die B tear strength 2.62-5.25 J/cm²; and specific gravity 1.100-1.150 Kg/m³.

The material should be selected based on the other factors needed, such as clarity, bondability and flowability. Table 9 is useful in determining the correct material to meet the needs of a particular design.

It is important to decide what type of bonding is necessary between the liquid injection molded silicone elastomer and the ETP substrate. There are three types of bonding available:

- In a static bond, the material is connected to the substrate by forces which are strong enough to hold the elastomer to the substrate for removal from the mold, but are weak enough such that the rubber can be removed without damage to the bulk material.

- The second adhesion option is a mechanical interlock. In this method, the ETP part is designed such that it has undercuts or flow channels which permit the flowing of the uncured liquid silicone elastomer, but prevent the cured material from being removed. This is a form of physical adhesion, and is useful where the part will see stresses that would remove a statically bonded elastomer. The undercuts can pose a technical challenge to the design of the ETP portion of the mold, additionally the bond is susceptible to leakage around the rubber portion at a microscopic level.

- Ultimate bonding occurs through the use of a chemical bond. This is possible through the use of the self-bonding liquid injection molded silicone elastomers. The bond achieved through this method results in >90% cohesive failure within the rubber.

The following data focus on the performance of the self-bonding liquid injection molded silicone elastomers when molded over various plastic substrates using a two shot molding process. The sample geometry was chosen to illustrate three distinct features commonly found in injection molded parts: o-ring gasket; a vertical interlocking seal; and variable nominal wall peel strip.

The parts were molded on a 150 ton two component ETP injection molding machine which was converted to a nETP/liquid silicone two shot machine. The part cycle times varied from several minutes to less than 40 seconds for the entire molding process, depending on the elastomer used. Adhesion data (table 10), are given in qualitative terms, corresponding to the amount of cohesive failure (excellent is >95% cohesive failure).

Conclusions

Siloxanes offer unique properties as elastomers, and there-

Table 9 - liquid injection molded selection guide

Properties	4200 Series	6000 Series	6745 Series	8040 Series	9000 Series
Duro. (Shore A)	90-70	10-70	45	40	70
Comp. set (+/-)					
As molded	-20	40-60	45	67	-25
Post baked	n/a	15-40	25-40	27	n/a
Self-bonding	No	No	No	Yes	Yes
FDA/Bio-Inert	No	Yes	Yes	No	In test
Clarity	Translucent	Clear to translucent	Translucent	Translucent	Translucent
Flowability	Medium	Medium	High	Medium	Medium

Table 10 - two-shot molding adhesion test using self-bonding grades

Self-bonding LIM elastomer/substrate matrix

	LIM 8040	LIM 9000
PPO/PA (Noryl GTX)	Excellent	Excellent
PBT (Valox)	Excellent	Excellent
PPA (Amodel)	Excellent	Excellent
PPO (Noryl)	Good	Good
PA (Nylon 6 glass-filled)	Good	Good
ABS	Good	Good
PPS (Supp)	Marginal	Marginal
PC (Lexan)	Poor	Poor
PC/ABS (Cycloxy)	Marginal	Marginal
PC (UV treated)	Excellent	Excellent
Aluminum	Excellent	Excellent
Steel (carbon, stainless)	Excellent	Excellent
Steel (galvanized)	Marginal	Marginal

fore are being used in increasing amounts for such applications. Liquid injection molded silicone materials have excellent physical and chemical properties which make them suitable alternatives to standard millable and pourable siloxane elastomers. New advances in liquid injection molded siloxane materials, including self-bonding, low compression set and controlled force deflection, address some previous issues that have limited the use of these systems in certain applications. The technique of two-component molding is particularly suited to a liquid silicone system, and advances in mold design have enabled a two-shot ETP/liquid injection molded elastomer system to be developed. Such a system offers extreme productivity, and when combined with the material advances, paints a bright future for liquid injection molded silicones.

References

1. F.S. Kipping, *Proc. Chem. Soc.* 20, 15 (1904).
2. J. March, "Advanced organic chemistry" Wiley-Interscience (1985).
3. B.B. Hardman and A. Torkelson, "Encyclopedia of chemical technology" Wiley & Sons, pp. 922-962 (1982).
4. U.S. Patent #3884866 Jeram et al.
5. J.L. Speier, Webster J.A. and Barnes G.H., *J. Am. Chem. Soc.* 79, 974 (1957).
6. B. Marciniec, "Comprehensive handbook of hydrosilylation" Pergamon Press (1992).

Medical Device Link.

The Online Information Source for the Medical Device Industry

Medical Plastics and Biomaterials Magazine | MPB Article Index

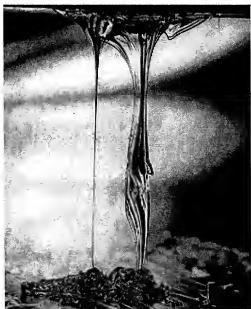
Originally published July 1997

SILICONES

Comparing Liquid and High Consistency Silicone Rubber Elastomers: Which Is Right for You?

Byron E. Wolf

Silicone elastomers have been employed for many years in the manufacture of medical devices, medical device components, and medical tubing. They have found use in a variety of critical-care and life-enhancing applications such as hydrocephalic shunts, pacemaker lead coverings, catheters, replacement finger joints, and pump diaphragms.



Low viscosity makes liquid silicone rubbers suitable for molding applications requiring complex, intricate molds.
Photos: Dow Corning Corp.

These elastomers are commercially available in two types: millable high consistency silicone rubber and pumpable liquid silicone rubber. For companies entering the device manufacturing market or expanding current operations, the type of silicone rubber selected will determine the equipment,

floor space, and labor requirements necessary to perform the device fabrication process.

ELASTOMER CHEMISTRY AND PROPERTIES

Silicone elastomers are proprietary compositions that contain silicone polymers, reinforcing and extending fillers, and cure ingredients.

Silicone Polymers. The polymers used in silicone elastomers are of the general structure depicted in Figure 1, where R represents -OH, -CH=CH₂, -CH₃, or another alkyl or aryl group, and the degree of polymerization (DP) is the sum of subscripts x and y. For high consistency silicone rubber elastomers, the DP is typically in the range of 5000 to 10,000. Thus, the molecular weight of the polymers--generally called gums--used in the manufacture of high consistency silicone rubber elastomers ranges from 350,000 to 750,000 or greater. In liquid silicone rubber elastomers, the DP of the polymers used typically ranges from 10 to 1000, resulting in molecular weights ranging from 750 to 75,000. The polymer systems used in the formulation of these elastomers can be either a single polymer species or a blend of polymers containing different functionalities or molecular weights. The polymers are selected to impart specific performance attributes to the resultant elastomer products.

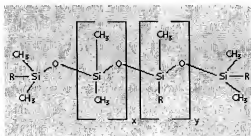


Figure 1. Chemical structure of typical silicone elastomers.

Reinforcing Fillers. Many manufacturers use reinforcing fillers to add strength to the finished elastomer product. Typically, these fillers are amorphous fumed silicas, although the use of precipitated silicas has increased in recent years. Particle sizes of standard reinforcing fillers normally fall within the range of 5 to 20 nm in diameter.

The reinforcement that occurs is the result of interaction between the polymer and the filler, whose surface typically has a silanol functionality. Because of the hydrogen bonding initiated by this silanol functionality, the interaction between polymer and filler can actually become so significant that it results in elastomers that are extremely stiff, giving the appearance of a cross-linked system. This phenomenon--commonly referred to in the industry as crepe--can be reversed, because it is possible to break down the hydrogen bonding through the addition of shear energy in the form of mixing or milling.

To achieve a level of polymer and filler interaction that provides a stable product while maintaining the reinforcing nature of the filler in the elastomer, a treatment, or pacification, of the silanol species on the reinforcing filler is necessary. This is typically carried out either through the addition of silanol-endblocked polydimethylsiloxane oligomers or via a capping reaction using reactive silanes or silazanes.

Extending Fillers. In order to impart particular performance attributes to silicone elastomers, extending fillers are sometimes employed. Examples of some common ones in the medical device industry include barium sulfate, used to produce radiopaque products, and titanium dioxide, a pigment that serves as a whitener.

Low viscosity makes liquid silicone rubbers suitable for molding applications requiring complex, intricate molds.

CURE MECHANISMS

Two major cure mechanisms are used in the manufacture of silicone rubber elastomer products: free radical cure and addition cure.

Free Radical Cure. Free radical cure systems employ peroxide catalysts that are either vinyl specific or nonspecific in nature. Adding heat causes the peroxide to decompose into two free radical-containing components, which then react with either an alkyl or a vinyl species along the polymer backbone, transferring the free radical to the silicone polymer. The cross-linking mechanism is terminated by the reaction of the free radical on the polymer chain with an alkyl species on another polymer chain.



There is little difference between liquid and high consistency silicones in terms of physical properties.

Nonspecific peroxides--such as bis(2,4-dichlorobenzoyl) peroxide or benzoyl peroxide--do not require the presence of vinyl or other unsaturated alkyl species in the polymers making up the elastomer formulations. These peroxide catalysts are commonly used in extrusion, but may also be appropriate for certain molding applications. Vinyl specific peroxide catalysts--for example, dicumyl peroxide or 2,5-bis(tert-butyl peroxy)-2,5-dimethyl hexane--require the presence of vinyl or other alkenyl species in the polymers contained in the elastomers. These vinyl specific catalysts do not perform well in extrusion applications, and are thus limited to use in molding.

A serious drawback to the use of peroxide cure in silicone materials is that it leaves residues in the cured elastomer, including acid by-products and polychlorinated biphenyls (PCBs). If the acid residue is not removed, it can manifest itself as a powder that forms on the part surface --a phenomenon commonly referred to as bloom. The application of an oven cure or postcure cycle is generally required to remove these by-products from the cured parts.

Despite this time-consuming postcure processing needed to eliminate residues, silicone elastomers incorporating the free radical peroxide cure are still widely used. Such elastomers are supplied either with the peroxide already formulated into the material, or uncatalyzed, in which case the fabricator adds the peroxide at the time of use. Examples of medical devices and components manufactured from peroxide cured, high consistency silicone rubber elastomers include tubing,

pacemaker-lead coverings, and hydrocephalic shunts. No liquid silicone rubber elastomers that use the free radical peroxide cure mechanism are commercially available. Table I lists typical properties obtained in high consistency silicone rubber elastomers cured via peroxide.

Addition Cure. The addition cure mechanism--known as hydrosilylation--involves the addition of a silicon hydride (*SiH) to an unsaturated carbon-carbon bond in the presence of a noble metal catalyst. The most commonly used of these hydrosilylation catalysts are based on platinum, although palladium and rhodium catalysts are also available. In order for the cure to occur, the silicone polymers contained in the elastomers must include a vinyl or other alkenyl functionality. Both high consistency and liquid silicone rubber products can employ the addition cure mechanism. Elastomers featuring this type of cure system are supplied as two-part kits: one part contains the catalyst species, the other a silicon hydridefunctional cross-linker and an inhibitor to provide working time once the two parts have been mixed.

The major advantage of addition cure for elastomers is that the cure reaction produces no by-products. Therefore, postcuring of the elastomer is normally not necessary, although a postcure cycle is sometimes performed to stabilize or enhance the properties of the finished product. Addition cure is inhibited by contact with materials containing amines, sulfur, phosphorous, tin complexes, peroxides, and peroxide by-products, and care must be taken to avoid contamination by any of these materials.

ASTM Reference	Test	High Consistency Silicone Rubber Grades *		
		A	B	C
D 792	Specific gravity	1.12	1.15	1.20
D 2240	Durometer hardness, Shore A (points)	36	49	66
D 412	Tensile strength (psi)	1280	1445	1150
D 412	Elongation (%)	800	665	600
D 624	Tear strength, die B (psi)	110	175	210

* Silicone Medical Grade ETR Elastomers (Dow Corning Corp.); A = 07-4530, B = 07-4550, C = 07-4565.

Table I. Typical properties obtained in high consistency silicone rubber elastomers cured via peroxide.

ASTM Reference	Test	High Consistency Silicone Rubber Grades *				
		D	E	F	G	H
D 792	Specific gravity	1.11	1.12	1.15	1.20	1.20
D 2240	Durometer hardness, Shore A (points)	24	35	49	64	76
D 412	Tensile strength (psi)	1255	1395	1550	1155	1170
D 412	Elongation (%)	1255	1170	900	895	670
D 624	Tear strength, die B (psi)	185	210	260	255	250

* Silicone Medical grade ETR Elastomers (Dow Corning Corp.); D = 07-4720, E = 07-4735, F = 07-4750, G = 07-4765, H = 07-4780.

Table II. Typical properties obtained in high consistency silicone rubber elastomers with addition cure.

ASTM Reference	Test	Liquid Silicone Rubber Grades *				
		I	J	K	L	M
D 792	Specific gravity	1.12	1.12	1.12	1.14	1.16
D 2240	Durometer hardness, Shore A (points)	27	39	43	49	59
D 412	Tensile strength (psi)	1205	1300	1230	1375	1376
D 412	Elongation (%)	830	705	515	690	515
D 624	Tear strength, die B (psi)	125	210	205	250	265

Table III. Typical properties obtained in liquid silicone rubber elastomers with addition cure.

Medical devices or components made from addition cured, high consistency silicone rubber elastomers include tubing, pump diaphragms, and catheters. Among the devices made from addition cured liquid silicone rubber elastomers are pump diaphragms, external male catheters, and wound-drainage bulbs. Typical properties obtained with an addition cure system for high consistency and liquid silicone rubber elastomers are listed in Tables II and III, respectively.

MATERIAL APPLICATIONS AND PROCESSING

As the data in Tables I, II, and III indicate, there is little difference between high consistency and liquid silicone rubber elastomers in terms of physical properties, regardless of the cure chemistry used. However, because of the disparity in the material types, the processing of these materials and their fabrication into medical devices vary significantly (see Figure 2).

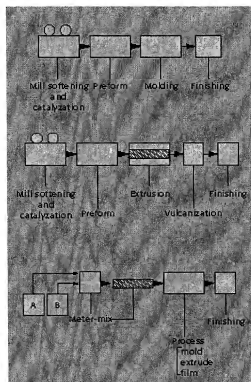


Figure 2. Comparison of processing steps in molding of high consistency silicones (top), extrusion of high consistency silicones (middle), and molding or extrusion of liquid silicones (bottom).

High consistency silicone rubber elastomers are ideal for use in extrusion because of the high viscosity polymers used in their formulation. The resulting products show very good green strength, which is the ability of the material to retain its extruded profile in the uncured state.

Liquid silicone rubbers, on the other hand, do not perform well in most standard extrusion applications because their viscosity is so low that they flow under little, if any, shear stress. Their utility in such applications is therefore limited to supported extrusion—that is, extrusion onto another substrate. Sleeving and membrane films are two examples of supported extrusion applications.

Both high consistency and liquid silicone rubbers are used extensively in the molding of elastomeric devices and device components. High consistency elastomers are typically molded using transfer or

compression molding techniques, both of which are labor-intensive. Liquid silicone rubbers are molded in highly automated injection molding systems. Given their significantly lower viscosity, liquid silicone rubber elastomers find utility in molding applications that require highly complex and intricate molds. Their ability to be molded in automated injection molding systems also lends itself to production runs involving large numbers of molded parts.

Processing High Consistency Silicone Rubbers. The processing of high consistency silicone rubber elastomers involves five steps: mill softening and catalyzation, preparation of a preform, extrusion or molding, vulcanization, and finishing.

Mill Softening and Catalyzation. The initial step in the processing of high consistency silicone rubber elastomers for use in either extrusion or molding applications is mill softening and catalyzation. This procedure reverses any "crepe hardening" that has occurred in the elastomer during storage in inventory at the supplier or fabricator. The milling is also used by fabricators to add peroxide catalyst to a free radical cured elastomer, if necessary, or to blend the two parts of an addition cured elastomer prior to fabrication.

Milling and catalyzation are not only labor-intensive, but also require the use of a two-roll mill, which costs approximately \$60,000 to purchase and install. The elastomer is passed through the mill numerous times until the compounded material is homogeneous, then removed in sheet form for further processing.

Preparation of a Preform. Once a high consistency elastomer is fully compounded, the next step in the fabrication process is the preparation of a preform. This requires no special equipment but is very labor-intensive, particularly in high volume applications that are almost continuous in nature. For extrusion and injection molding applications, the preform is prepared simply by cutting the elastomer sheet into strips, which are used to feed the extruder. For transfer molding operations, the preform is typically cut with a die-cutter into a plug that will fit in the transfer reservoir of the transfer press. For compression molding applications, the process is slightly more complicated, since the preform must be cut in the basic geometric configuration of the final part.

Extrusion. For high consistency elastomers, extrusion is accomplished using a single-screw extruder. The preformed strips are fed to the extruder from a roller feed wheel into the extruder barrel, and the elastomer is extruded through a die and mandrel assembly to form the desired profile. It is also possible to carry out supported extrusion with high consistency silicone elastomer. This is achieved by fitting a crosshead assembly onto the extruder, passing the supporting geometry through the crosshead, and extruding a layer of silicone rubber over it.

The cost of an extruder appropriate for medical applications is approximately \$100,000, including installation. However, most extrusion system fabricators equip their machines with laser micrometers and feedback controllers to monitor product quality, an enhancement that adds significantly to the cost of setting up an extrusion process. In addition, extrusion can be considered labor-intensive, since it requires the presence of an operator at all times to ensure that the extruder has a constant supply of elastomer and is operating properly.

Molding. High consistency silicone applications vary with the type of molding equipment used. Transfer and injection molding processes require operational personnel to load the elastomer into the equipment and to demold the finished parts. For compression molding, operators must place preforms in all the individual cavities in each mold. Because of the relatively slow cure cycles employed with high consistency elastomers, it is possible for the molds to have large numbers of cavities. The cost of installing a transfer or injection molding press is approximately \$1000 to \$2000 per ton of clamp force. Compression molding presses are considerably less expensive.

Vulcanization. Vulcanization of the extruded product is typically achieved with hot-air vulcanizing ovens, or HAVs. These HAVs are available in both horizontal and vertical configurations. In the horizontal models, the extruded profile is laid on a continuous belt and passed through the oven, where hot air is forced over the extrudate to initiate the vulcanization mechanism. In the vertical oven configuration, the HAV is equipped with a variable-speed drum at the top to pull the extruded profile upward through the oven, where it is cured. The cost of a typical HAV oven is approximately \$30,000. Other types of vulcanization ovens employed include radiant-heat ovens and steam autoclave ovens.

Finishing. The degree of finishing required depends on the specific application. For extrusion processes, finishing involves visual inspection and cutting of the tubing into specified lengths. If the tubing has been cured with a peroxide, the finishing process also entails an oven postcure to remove peroxide by-products. For molding applications, finishing includes the trimming or deflashing of the molded parts, often using die-cutting machinery to cut the individual parts from a larger molded sheet, and any oven postcuring that is necessary. In addition to wasting material, finishing of high consistency silicones is labor-intensive and requires additional equipment such as ovens and die-cutters. However, this equipment is relatively inexpensive to purchase.

Processing Liquid Silicone Rubbers. In contrast to high consistency materials, the processing of liquid silicone rubber elastomers requires only three steps: meter-mixing, molding, and finishing. The major advantage of the liquid silicone rubber system is that it is designed to be used in highly automated, closed systems, with very little labor required once the system has been put into operation.

Meter-Mixing. The initial step, meter-mixing, is performed using pneumatic pail or drum pumps. These pumps deliver the two parts of the liquid silicone rubber--at a 1:1 ratio--to a multielement static mixer, where the two parts are airlessly mixed until they are homogeneous. Meter-mix systems have improved tremendously over the years, and also allow for the controlled incorporation of other additives, such as pigments. The cost of a meter-mix system is approximately \$15,000 to \$25,000.

Molding. The molding of liquid silicone rubbers is accomplished using modified plastic injection molding machines. These machines are highly automated and, once operational, require almost no labor to operate. Such equipment costs approximately \$1000 to \$2000 per ton of clamp force required. The greatest expense in the molding of liquid silicone rubber elastomers is the cost associated with the design and production of the mold itself. Depending on complexity, a mold can cost from a few thousand to several hundred thousand dollars. The recent introduction by several suppliers of all-electric molding machines bodes well for the future of liquid silicone rubber injection molding in the medical device industry, since these units can be used in cleanroom environments, from which typical hydraulic machines are precluded because of potential contamination by hydraulic fluids.

Finishing. For typical applications, finishing operations are not necessary in liquid silicone rubber injection molding systems. The molds, if properly tooled, produce minimal flash, eliminating the need for trimming. Likewise, because these materials use the addition cure mechanism, a postcure cycle is not required, although it may be performed to stabilize or enhance the properties of the cured parts.

CONCLUSION

The selection of the right type of silicone rubber elastomer for a specific use is largely a matter of personal preference and availability of equipment. There is little observable difference between

peroxide cured high consistency silicone rubbers, addition cured high consistency silicone rubbers, and liquid silicone rubbers in terms of physical property performance. However, the materials differ significantly in terms of the processing necessary to fabricate medical devices and components.

For extrusion applications, high consistency silicones are the material of choice. Liquid silicone rubbers do not exhibit the green strength necessary to maintain extruded profiles until they can be vulcanized. Either peroxide or addition cure systems can be used, although peroxide systems do require an additional postcure step.

For molding applications, either high consistency or liquid silicones are acceptable. For facilities already processing high consistency elastomers, continuing with the same type of material may be the most efficient and cost-effective course of action. However, new operations entering the marketplace should give serious consideration to using liquid silicone rubber, because the capital costs and labor involved are significantly lower than those associated with the processing of high consistency material. Whatever the choice, an extensive knowledge base exists to provide technical assistance, and material and equipment suppliers alike are available to share their expertise and help ensure manufacturing success.

BIBLIOGRAPHY

Clarson SJ, and Semlyen JA, Siloxane Polymers, Englewood Cliffs, NJ, PTR Prentice Hall, 1993.

Morton M (ed), Rubber Technology, 3rd ed, New York, Van Nostrand Reinhold, 1987.

Byron E. Wolf is a development specialist with Dow Corning Corp. (Midland, MI), where his responsibilities include leading the R&D program for liquid silicone rubber elastomers in the company's Healthcare Industries Science and Technology group. He is also an adjunct faculty member in chemistry and chemical engineering at the South Dakota School of Mines and Technology.

Copyright ©1997 Medical Device & Diagnostic Industry

© 1996-2009 Canon Communications



[Home](#) | [About Us](#) | [Contact us](#) | [Site map](#) | [Subscribe](#) | [Privacy](#) | [Advertise](#)

Report 137

ISSN: 0889-3144

Silicone Elastomers

Peter Jerschow
(Wacker-Chemie GmbH)

Volume 12, Number 5, 2001

Rapra Review Reports

*Expert overviews covering the science and
technology of rubber and plastics*

RAPRA
TECHNOLOGY LTD.

Supplied free of charge

1 Introduction

Silicone elastomers are elastic substances which contain linear silicone polymers crosslinked in a 3-dimensional network.

In most cases this network also contains a filler which acts as a reinforcing agent or as an additive for certain mechanical, chemical or physical properties.

In general all silicones (usually we refer to silicones as polydimethyl siloxanes) are noted for their high thermal stability, biocompatibility, hydrophobic nature, electrical and release properties. When silicones are crosslinked to form a silicone rubber their characteristic properties are still prevalent. Hence silicone elastomers can be widely used in a great variety of applications. Some examples are shown in Table 1. These will be described in more detail when concentrating on specific groups of materials and applications.

We will not refer too much to silicone adhesives in this article, in spite of the fact that they form silicone elastomers when being cured. These materials have been referred to extensively in the literature (a.1, a.2).

1.1 Nomenclature

The nomenclature classifies silicone elastomers by their curing mechanism and curing conditions. Silicone rubbers are essentially divided into two groups of materials, i.e., room temperature vulcanising (RTV) and high temperature vulcanising (HTV). RTV systems are able to cure at room temperature and HTV systems at temperatures well above 100 °C. A number in the name indicates the number of components that upon mixing will form a curable composition, e.g., RTV-2.

HTV rubbers are mainly so-called solid silicone rubbers. They have a very high viscosity in the uncured state and appear as solids. This behaviour has also led to the creation of the term 'High Consistency Rubber' (HCR).

Approximately 25 years ago a new group of materials appeared that was intended for processing in injection moulding machines. Because of their low viscosity and paste-like behaviour they were named liquid silicone rubbers (LSR) or simply liquid rubbers (LR). It is common to use LSR or LR as an abbreviation instead of HTV, even though they vulcanise at high temperatures as in the case of solid silicone rubbers.

Table 1 Brief overview of applications for silicone elastomers

Application area	Applications
Automotive	Exhaust pipe hangers Crank shaft seals Radiator seals Ignition cables Connector seals Spark plug boots
Medical	Catheters Respiration masks Various valves (e.g., dialysis apparatus) Anaesthetic tubing (composite) Body contact electrodes X-ray opaque stents Various pads
Wire and cable	Wear resistant cables Instrument cables Safety signal cables Safety power cables Battery cables Economy grade cables Heat resistant cables Cable sheaving, wear resistant Cables from silicone rubber pellets

continues...

1 Introduction

Silicone elastomers are elastic substances which contain linear silicone polymers crosslinked in a 3-dimensional network.

In most cases this network also contains a filler which acts as a reinforcing agent or as an additive for certain mechanical, chemical or physical properties.

In general all silicones (usually we refer to silicones as polydimethyl siloxanes) are noted for their high thermal stability, biocompatibility, hydrophobic nature, electrical and release properties. When silicones are crosslinked to form a silicone rubber their characteristic properties are still prevalent. Hence silicone elastomers can be widely used in a great variety of applications. Some examples are shown in Table 1. These will be described in more detail when concentrating on specific groups of materials and applications.

We will not refer too much to silicone adhesives in this article, in spite of the fact that they form silicone elastomers when being cured. These materials have been referred to extensively in the literature (a.1, a.2).

1.1 Nomenclature

The nomenclature classifies silicone elastomers by their curing mechanism and curing conditions. Silicone rubbers are essentially divided into two groups of materials, i.e., room temperature vulcanising (RTV) and high temperature vulcanising (HTV). RTV systems are able to cure at room temperature and HTV systems at temperatures well above 100 °C. A number in the name indicates the number of components that upon mixing will form a curable composition, e.g., RTV-2.

HTV rubbers are mainly so-called solid silicone rubbers. They have a very high viscosity in the uncured state and appear as solids. This behaviour has also led to the creation of the term 'High Consistency Rubber' (HCR).

Approximately 25 years ago a new group of materials appeared that was intended for processing in injection moulding machines. Because of their low viscosity and paste-like behaviour they were named liquid silicone rubbers (LSR) or simply liquid rubbers (LR). It is common to use LSR or LR as an abbreviation instead of HTV, even though they vulcanise at high temperatures as in the case of solid silicone rubbers.

Elastomers · Silicone rubbers · Nanocomposites · Carbon nanotubes

In the recent years, carbon nanotubes have been the subject of a great scientific interest on account of their exceptional properties. Their use in polymer-based nanocomposites remains limited due to problems encountered with their dispersion and interaction in the host matrix. Nevertheless, an outstanding affinity of carbon nanotubes towards poly(dimethylsiloxane) (PDMS) has been demonstrated. Tiny amounts of multiwall carbon nanotubes are required to bring significant changes in the mechanical, electrical and thermal properties of PDMS.

Kohlenstoff Nanoröhrchen: außergewöhnliche Füllstoffe für Silikonkautschuk

Elastomere · Silikonpolymere ·
Nanoverbundstoffe · Kohlenstoff
Nanoröhrchen

Seit einigen Jahren erfreuen sich Kohlenstoff Nanoröhrchen (CNT), ihrer außergewöhnlichen Eigenschaften wegen, eines großen wissenschaftlichen Interesses. Ihre Verwendung in polymeren Verbundwerkstoffen ist begrenzt durch die bei der Dispersion und der Wechselwirkung mit der Matrix auftretenden Schwierigkeiten. Nichts desto Trotz wird eine besondere Affinität der CNTs zu Poly(dimethylsiloxan) (PDMS) festgestellt. Geringe Mengen mehrwandiger CNTs werden benötigt um mechanische, elektrische und thermische Eigenschaften von PDMS zu verbessern.

Carbon Nanotubes: Exceptional Reinforcing Fillers for Silicone Rubbers

Poly(dimethylsiloxane) (PDMS) has long been known to be a high performance material on account of its high thermal stability and its very low glass transition temperature. But in order to take advantage of these properties, PDMS requires, in most applications, to be reinforced by fillers to improve its mechanical properties which are weak in the unfilled state.

PDMS and silica particles have been successfully used to prepare composites with greatly improved properties such as strength, stiffness and wear resistance [1]. The effectiveness of the reinforcing agent has been shown to depend on several parameters including filler morphology and especially surface characteristics [2]. Actually most studies ascribe the increased stiffness and strength, imparted by silica to the elastomeric matrix, to hydrogen bonding between hydroxyl groups on the silica surface and PDMS chains.

The last few years have seen the extensive use of nanoparticles because of the small size of the filler and the corresponding increase in the surface area, allowing to achieve the required mechanical properties at low filler loadings. A reinforcement technique based on the incorporation of silica through a sol-gel in situ precipitation was developed by Mark et al. [3-8] for essentially silica filling of silicone rubbers. The sol-gel process prevents the formation of large silica aggregates frequently obtained by the usual blending of the filler into the polymer prior to its cross-linking into an elastomeric network and allows good control of the size and distribution of the particles within the matrix [9]. Other nanofillers, having large surface areas and aspect ratio, such as layered silicates or carbon nanotubes, are of prime interest as reinforcing agents for elastomeric matrices. If delamination of the stacked clay nanoplatelets or breaking down of bundles of aggregated carbon nanotubes are achieved, significantly enhanced properties are expected with regard to the unfilled polymers or conventional composites.

In the recent years, carbon nanotubes have attracted considerable interest on account of their remarkable mechanical and electrical properties. Carbon nanotubes consist of one or more concentric graphitic cylinders with typical diameters ranging from about 1 to tens of nanometers and lengths of several micrometers (even millimeters or centimeters). The key parameters which determines the usefulness of carbon nanotubes as reinforcing fillers for elastomers are their effective dispersion within the matrix and the interfacial interactions between the polymer and the filler. Actually, one of the main problem with carbon nanotubes is their strong tendency to form agglomerates which act as defects in the composite and limit the mechanical performance of the resulting material. Despite the significant advances made on the processing of polymer composites, up to now poor dispersion and lack of interfacial adhesion between the tubes and the polymer matrix have been shown to limit the full realization of the filler properties for a nanoscale reinforcement. Even if improvements in the composite tensile stiffness are observed, strain at break is often degraded as a result of the presence of bundles within the polymer matrix [10-14].

Some studies report the use of carbon nanotubes in silicone based elastomers. Frogley et al. [15] analyzed the mechanical properties of a silicone rubber reinforced with single-wall carbon nanotubes (SWNTs). The initial modulus is shown to increase sharply

Authors

L. Bokobza, M. Rahmani, Paris
(France)

Corresponding author:
Liliane Bokobza
ESPCI
Laboratoire PMMD
10 rue Vauquelin
75231 Paris Cedex, France
E-mail: Liliane.Bokobza@espci.fr

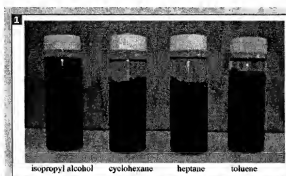
with the filler content but a reduction in ultimate strain is obtained. Another study of the same group proves by atomic force microscopy the complete and spontaneous wetting of a nanotube by a liquid of PDMS [16]. Park et al. [17] mention a sudden increase in viscosity when MWNTs and the hardener were mixed and added into the silicone rubber at maximum filler contents limited to 0.7 wt% on account of retardation effects on the cross-linking process at concentrations approaching 1 wt%. A spectacular increase in viscosity has also been observed upon adding MWNTs to the unfilled PDMS at filler loadings between 0.1 wt% and 0.3 wt% [18]. This increase in viscosity at extremely low filler content was assumed, through modeling studies, to be connected to strong CH- π interactions between the PDMS methyl groups and the π -electron-rich surface of the carbon nanotube. This unexpected affinity of CNTs for PDMS opens the way to the production of new materials with highly improved mechanical and electrical properties. Taking advantage of our knowledge of the molecular mechanisms of reinforcement of PDMS by different types of fillers [1], we decided to carry out an analysis of effects provided by the incorporation of carbon nanotubes in silicone rubbers.

In this paper, we report investigations performed on PDMS filled with multiwall carbon nanotubes (MWNTs). Synthetic aspects as well as mechanical, electrical and thermal properties are discussed. Additionally, Raman data are provided.

Experimental section

Synthesis of the unfilled networks

Unfilled PDMS networks can be obtained by end-linking polymer chains by means of a multifunctional cross-linking agent. This type of process using bifunctional polymers of known molecular weight reacting with adequate multifunctional reagent are widely used to obtain elastomeric networks with structures expected to be as close as possible to ideal. Samples can be obtained by the hydrosilylation reaction (i.e., the addition of a silyl function -SiH of precursor chains of hydride-terminated PDMS to an unsaturated C=C bond of the cross-linking molecule [19] or the addition of vinyl functional polymers to a SiH group of a tetrafunctional siloxane [9]). In both cases, the hydrosilylation reaction is catalyzed by a platinum complex (i.e., platinum-divinyltetramethyldisiloxane). Alternatively, terminal silanol functional PDMS are able to condense to



1 MWNTs dispersions at 0.01 wt% in various solvents one week after their preparation

alkoxy systems (the most widely used being tetraethoxysilane or TEOS) under a tin compound catalyst. Nevertheless the reaction between hydroxyl-terminated PDMS and TEOS is difficult to control and, to be efficient, requires, as often reported in the literature [20, 21], larger amounts of TEOS than the stoichiometric equivalent. A typical synthesis started from OH-terminated precursor chains is described below.

Hydroxyl-terminated PDMS ($M_w = 18000$) supplied by Gelest is mixed for half an hour with TEOS, in excess of 50%, and used here as the cross-linking agent. A small amount of stannous-2-ethyl-hexanoate used as catalyst, is then added to the mixture under magnetic stirring just for 5 minutes to avoid cross-linking reaction during mixing. The reacting mixture is slowly cast into a Teflon mold and left a few minutes at room temperature then at 80 °C for one day for complete curing. The films are extracted with toluene for 72 hours to remove any unreacted materials. The sol fractions are between 4 and 5%.

In the previous studies, PDMS networks were synthesized by using a stoichiometric balance between ethoxy groups of the tetrafunctional alkoxy silane cross-linker and the hydroxyl chain ends of the hydroxyl-terminated PDMS precursor chains in order to get model networks characterized by constant junction functionality and known molecular weight between cross-links (close to the number-average molecular weight of precursor chains) [3-8]. In fact, networks prepared at stoichiometric conditions have an elastic modulus lower than that deduced from the molecular weight between cross-links and great soluble fraction (around 10%). This may be due to the volatility of TEOS thus reducing the amount of cross-linker required for the alkoxy-functional condensation reaction. Much greater ratios of cross-linker functions to chain ends than that required by stoichiometry have already been used in the literature [20, 21] but in

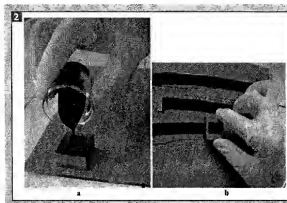
our case, we carried out a systematic study of the effect of excess of TEOS on the mechanical properties of networks synthesized from OH-terminated chains. A 50% excess (and not higher values as already reported) are enough to ensure correct modulus and reasonable soluble fraction.

Procedures for composite preparation

Multiwall carbon nanotubes (MWNTs) were purchased from Nanocyl S.A. (Belgium). In this study, we have used the Nanocyl 7000 series (purity : 90%) produced via the catalytic carbon vapor deposition process without any further purification. Their average diameter and length are around 10 nm and 1.5 μ m respectively and their surface area between 250 and 300 m² g⁻¹.

Since PDMS is a fluid liquid before the cross-linking reaction, carbon nanotubes can be directly sonicated into the polymeric medium. Nevertheless, solution processing in a suitable solvent of the composites yields better nanotube de-aggregation and dispersion. As already mentioned, a uniform and homogeneous dispersion is required for an optimal utilization of the nanotubes as efficient fillers. Different solvents have been tested and it appears that dispersing the nanotubes in isopropyl alcohol by ultrasonication gives a stable dispersion one week after the preparation (Fig. 1).

Nanocomposites were prepared using the following protocol: first the appropriate amount of MWNTs was dispersed into isopropyl alcohol (0.1 mg/ml) by sonicating the suspension for 30 min using a Vibra-Cell VCX 500 operating at 40% amplitude with on and off cycles respectively equal to 5 and 1 seconds. Then the dispersion was added to PDMS and the system was mechanically mixed until total evaporation of the solvent. The cross-linking agent is then introduced under magnetic stirring for around 20 minutes and after addition of the catalyst and further mixing, the uncured mixture is poured into a manual applicator with 4 pre-



2 Film casting from a PDMS/MWNTs dispersion

set film thicknesses (Fig. 2a). It has to be mentioned that the final mixture displays, with regard to the unfilled PDMS, a very strong increase in viscosity indicating interfacial interactions between polymer chains and carbon nanotubes. Despite the increase in viscosity, strips of thickness around $400\mu\text{m}$ are easily drawn across a glass plate recovered with a Teflon film and left at 80°C for one night for complete curing (Fig. 2b).

Methods of characterization

Measurements of mechanical properties and equilibrium swelling were carried out in the usual manner.

Stress-strain measurements reported here were carried out by simply stretching strips of $50 \times 5 \times 0.4\text{mm}^3$ between two clamps by means of a sequence of increasing weights attached to the lower clamp. The distance between two marks is measured with a cathetometer after allowing sufficient time (10 min after adding a weight) for equilibration.

To determine the equilibrium swelling of the vulcanizate, a sample of $20\text{mm} \times 10\text{mm} \times 0.4\text{mm}$ was put into cyclohexane. After 72h at room temperature, the length and width of the sample were measured with a caliper square. The weight swelling ratio, Q , was determined from the lengths of the sample in the unswollen and swollen states.

Differential scanning calorimetry measurements (DSC) were carried out on a TA DSC 2820 instrument from room temperature to -150°C with a cooling rate of $1.5^\circ\text{C}/\text{min}$ under N_2 atmosphere.

Electrical resistivity measurements were determined on samples of $10 \times 20 \times 0.4\text{mm}^3$ by measuring their resistance on a high resistance meter (Keithley 6517A) between two conductive rubber electrodes with an alternative voltage of 1 V. This alternative

voltage is needed to avoid a background current effect. The measured resistances R were then converted into volume resistivity ρ by using this equation:

$$\rho = \frac{RS}{d} \quad (1)$$

where S is the cross-sectional area perpendicular to the current and d the thickness of the sample between the two electrodes. Infrared spectra were obtained on a Tensor 27 from Bruker equipped with a Golden Gate single reflection attenuated total reflectance (ATR) system. ATR spectra were recorded with a resolution of 4cm^{-1} and an accumulation of 32 scans.

The Raman spectra were recorded in the backscattering geometry on a Labram I (Jobin-Yvon, Horiba Group, France) microspectrometer in conjunction with a confocal microscope. To avoid any thermal photochemical effect, we have used a minimum intensity laser power on sample of $370\mu\text{W}$ with the 514.5nm incident line from an Ar-Kr laser from Spectra Physics. Detection was achieved with an air cooled CCD detector and a $1800\text{grooves}/\text{mm}$, giving a spectral resolution of 4cm^{-1} . An acquisition time of 120 s was used for each spectrum. The confocal aperture was adjusted to $200\mu\text{m}$ and a $50\times$ objective of 0.75 numerical aperture was used.

Results and discussion

With regard to the unfilled matrix, significant increases in mechanical properties are observed upon addition of small amounts of MWNTs (Fig. 3). The elastic modulus of the unfilled network, found equal to 0.136MPa from the slope of the nominal stress against $(\alpha - \alpha^\circ)$ is in perfect agreement with the theoretical one ($\rho RT/M_c$) calculated from the molecular weight between cross-links, M_c .

A great deal of theoretical work has been carried out in order to model the mechanical properties of rod-like particle reinforced composites. The Guth equation [22] based on the aspect ratio, f , and volume fraction, ϕ , of filler, predicts a strong increase in modulus at high volume fraction:

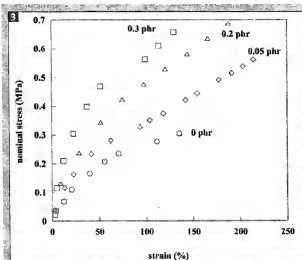
$$E = E_0 (1 + 0.67f\phi + 1.62f^2\phi^2) \quad (2)$$

(E and E_0 are the moduli of the composite and the unfilled elastomer, respectively). The Halpin-Tsai model [23] yields, for aligned fibre composites and in conditions where the modulus of the fiber, E_f , is much higher than that of the unfilled matrix (as in elastomeric composites):

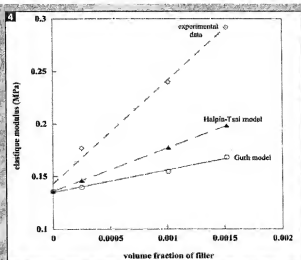
$$E = E_0 (1 + 2f\phi)/(1 - \phi) \quad (3)$$

The dependence of the experimental elastic modulus on the volume fraction of filler is much higher than that predicted by the two mechanical models using $f = 150$ from the dimensions of the individual nanotubes (Fig. 4). Filler-rubber interactions could explain the large difference between the mechanical models and the tensile behavior of our samples.

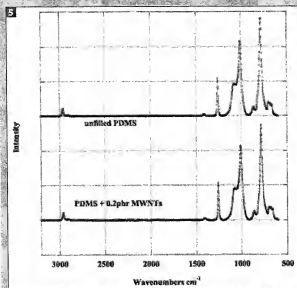
$\text{CH}-\pi$ interactions were suggested to be involved between the π -electron-rich surface of the carbon nanotube and the PDMS methyl groups [18]. This type of interactions widely discussed by Nishio [24] was mostly evidenced by infrared spectroscopy. These weak hydrogen bonds are expected to affect the vibrational frequencies of the methyl group modes. CH_3 asymmetric and symmetric stretching vibrations are respectively located at 2964 and 2905cm^{-1} in the ATR-infrared spectrum of the unfilled PDMS while the CH_2 bending vibrations appear at 1412 and 1257cm^{-1} . These absorption bands do not suffer any shift in the ATR spectrum of PDMS with carbon nanotubes (Fig. 5). A same conclusion can be drawn from the analysis of the Raman spectra where the bands associated with the stretching modes of the methyl groups are well-defined and more intense than in the ATR spectra (Fig. 6). The only change observed in the Raman spectra concerns the band located at 712cm^{-1} for the unfilled material. This band which is assigned to the Si-C symmetric stretching [25, 26] is shifted at 709cm^{-1} in the Raman spectrum of the composite. At the present time, we do not know whether this particular vibration reflects a change in polymer conformation or not but if some interaction exists between the PDMS chain and the nanotube surface, it does not seem to affect the stretching and bending modes of the methyl groups.



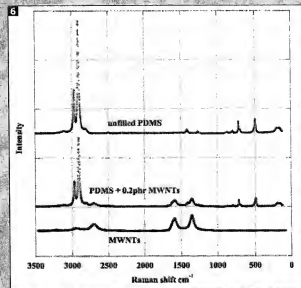
3 Stress-strain curves for pure PDMS (formed from silanol terminated precursor chains of molecular weight 18000) and for PDMS/MWNTs composites



4 Experimental elastic modulus as a function of filler volume fraction and comparison with predictions of the Guth and Halpin-Tsai models



5 ATR spectra of unfilled and filled PDMS



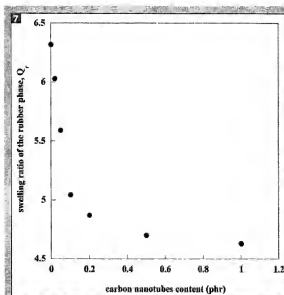
6 Raman spectra of unfilled and filled PDMS and pure carbon nanotubes

Also reported in Figure 6 is the Raman spectrum of pure MWNTs which exhibits the typical D, G and G' bands respectively located at 1351, 1587 and 2697 cm^{-1} . These bands are shifted to 1354, 1592 and 2700 cm^{-1} in the PDMS/MWNTs composite. High-frequency shifts in Raman bands of carbon-based fillers have often been observed when carbon black particles or nanotubes are incorporated into a polymer matrix [27, 28].

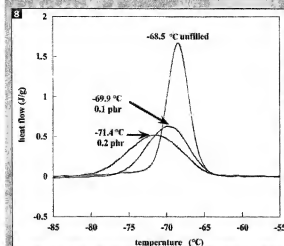
The degree of adhesion between polymer chains and filler particles can be evaluated from equilibrium swelling of the compos-

ites in good solvents. The extent of swelling at equilibrium is reduced in the case of adsorption of polymer chains on particle surfaces, and may be enhanced with non-adhering fillers due to a dewetting of the particles and vacuole formation [29]. As seen in Fig. 7 for PDMS/MWNTs composites, the equilibrium swelling ratio of the rubber phase in cyclohexane, Q_e , decreases with increasing amount of carbon nanotubes, indicating a pronounced restriction in swelling in the filled samples. Such experiments are generally used to estimate the total crosslinking density and the polymer-filler at-

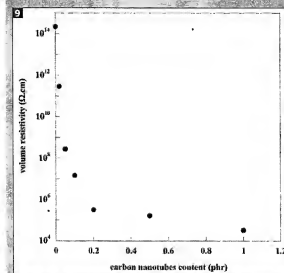
tachments. Q_e is equal to $(Q - \phi) / (1 - \phi)$, where Q is the equilibrium swelling ratio of the composite ($Q = V/V_0$, V being the volume of the swollen sample and V_0 that of the dry sample) and ϕ is the volume fraction of filler in the dry state. An alternative explanation to the swelling restriction would be to consider occluded rubber in addition to the actual volume occupied by the carbon nanotubes. This interpretation is not unrealistic because during the composite processing, a certain amount of polymer could be entrapped inside the nanotube bundles.



7 Dependence of rubber phase swelling on the amount of carbon nanotubes



8 Dependence of the crystallization peak of PDMS on the amount of carbon nanotubes



9 Volume resistivity against nanotubes loading for PDMS composites

Fillers can modify the morphology of the matrix by acting as nucleating agents and promoting the crystallization process of the polymer or they may also lead to a decrease in crystallinity. Several reports indicate that the addition of carbon nanotubes enhances the degree of crystallinity of polymers such as polypropylene [30-32], nylon-6 [33] or poly(ϵ -caprolactone) [34]. In a recent study of nanocomposites of high-density polyethylene and carbon nanotubes, Trujillo et al. [35] report an increase in the crystallinity degree due to the nucleation effect of carbon nanotubes on the polymer matrix and a strong reduction in crystallinity at higher CNT content (25 % CNT or more) due to confinement effects of polymer chains at the interfaces. In PDMS/SiO₂ composites where strong interactions exist between the matrix and the fillers, the rate of crystallization has been shown to decrease with an increase in the filler content [9, 36, 37]. It is assumed that the polymer in the interfacial region does not crystallize and according to Aranguren [36], the curing process also restricts the ordering of the chains to form a crystal and thus the percentage of crystallinity. In a recent study of Xu et al. [38] on the thermal properties of single walled carbon nanotube (SWNTs)-silicone nanocomposites, it is shown that the addition of nanotubes in the polymer seriously hinder the curing of the silicone elastomer and that the hindrance increases with increasing concentration of SWNTs and the quality of their dispersion in the matrix. It is claimed that the better the quality of dispersion, the more serious the retardation was. On the other hand, their cooling DSC data show that SWNTs significantly enhance the percentage of the melt crystallisation of pure silicone elastomer and better crystallinity is obtained for better dispersion of the nanotubes in the polymer. The authors suggest that SWNTs behave in their systems as nucleation sites, which enhances the crystallinity. Our results disagree with the above observations since a decrease in the temperature of crystallization is obtained as in high reinforcing silicas (Fig. 8).

One of the major attribute of carbon nanotubes is to provide electrical conduction at a lower filler loading than other carbon materials. The electrical conduction process depends on several parameters such as processing techniques used to mix fillers with rubbers, filler content and filler characteristics such as particle size, structure as well as polymer-filler interactions which determine the state of dispersion. The resistivity as a function of the filler loading displays

the typical insulator-conductor transition corresponding to the formation of a conductive path throughout the sample reaching the so-called percolation threshold (Fig. 9). It can be seen that this transition occurs at a filler loading of 0.05 phr which is very low with regard to previous results related to hydrocarbon rubbers where it was shown that carbon nanotubes form the interconnecting filler network between 2 and 3 phr [28]. This large reduction in the amount of conductive inclusions is particularly valuable for the elaboration of electrically conductive silicones in commercial applications.

Conclusion

Significant changes in physical properties of silicone rubbers are observed by addition of carbon nanotubes at extremely low filler content. Although the nature of the interaction between the nanotube surface and the polymer chains is not clearly understood, a noticeable increase in mechanical properties is obtained even at a tiny loading of 0.05 wt%. This filler content also corresponds to the formation of an electrically percolated network.

References

- [1] L. Bokobza, *Journal of Applied Polymer Science*, **93** (2004) 2095.
- [2] L. Bokobza, *Macromolecular Materials and Engineering*, **289** (2004) 607.
- [3] D. W. McCarthy, J. E. Mark and D. W. Schaeffer, *Journal of Polymer Science: Part B: Polymer Physics*, **36** (1998) 1167.
- [4] S. Wang, P. Xu and J. E. Mark, *Rubber Chemistry and Technology*, **64** (1991) 746.
- [5] J. E. Mark, *Journal of Applied Polymer Science: Applied Polymer Symposium*, **50** (1992) 273.
- [6] J. Wen and J. E. Mark, *Rubber Chemistry and Technology*, **67** (1994) 806.
- [7] D. W. McCarthy, J. E. Mark, S. J. Clarson and D. W. Schaeffer, *Journal of Polymer Science: Part B: Polymer Physics*, **36** (1998) 1191.
- [8] J. M. Breiner, J. E. Mark and G. Beaucage, *Journal of Polymer Science: Part B: Polymer Physics*, **37** (1999) 1421.
- [9] L. Dewimille, B. Bresson and L. Bokobza, *Polymer*, **46** (2005) 4135.
- [10] L. Bokobza and M. Kolodziej, *Polymer International*, **55** (2005) 1090.
- [11] M. Kolodziej, L. Bokobza and J.-L. Bruneel, *Composite Interfaces*, **14** (2007) 215.
- [12] L. Bokobza and C. Belin, *Journal of Applied Polymer Science*, **105** (2007) 2054.
- [13] L. Bokobza and N.-E. El Bounia, *Composite Interfaces*, **15** (2007) 9.
- [14] L. Bokobza, *Polymer*, **48** (2007) 4907.
- [15] M. D. Frogley, D. Ravich and H. D. Wagner, *Composites Science and Technology*, **63** (2003) 1647.
- [16] A. H. Barber, S. R. Cohen and H. D. Wagner, *Physical Review Letters*, **92** (2004) 186103.
- [17] I.-S. Park, K. J. Kim, J.-D. Nam, J. Lee and W. Yim, *Polymer Engineering and Science*, **47** (2007) 1396.
- [18] A. Beigzadeh, M. Linars, M. Dewalckenaere, P. Degée, M. Claes, D. Beljonne, R. Lazzaroni and P. Dubois, *Advanced Materials*, **20** (2008) 1003.
- [19] S. Besbes, I. Cernelli, L. Bokobza, L. Monnerie, I. Bahar, B. Erman and J. Herz, *Macromolecules*, **25** (1992) 1949.
- [20] H. Takeuchi and C. Cohen, *Macromolecules*, **32** (1999) 6792.
- [21] D. F. Schmidt, F. Clément and E. P. Giannelis, *Adv. Funct. Mater.*, **16** (2006) 417.
- [22] E. Guth, *Journal of Applied Physics*, **36** (1945) 20.
- [23] J. C. Halpin, *Journal of Composite Materials*, **3** (1969) 732.
- [24] M. Nishio, *CrytEngComm*, **6** (2004) 130.
- [25] L. Jayes, A. P. Hard, C. Séné, S. F. Parker and U. A. Jayasooriya, *Anal. Chem.*, **75** (2003) 742.
- [26] S. C. Bae, H. Lee, Z. Lin and S. Granick, *Langmuir*, **21** (2005) 5685.
- [27] T. McNally, P. Pötschke, P. Halley, M. Murphy, D. Martin, S. E. J. Bell, G. P. Brennan, D. Bein, P. Lemoine, J. P. Quinn, *Polymer*, **46** (2005) 8222.
- [28] L. Bokobza, M. Rahmani, C. Belin, J.-L. Bruneel, N.-E. El Bounia, *Journal of Polymer Science: Part B: Polymer Physics*, **46** (2008) 1939.
- [29] G. Kraus, *Advances In Polymer Science*, **B** (1971) 155.
- [30] E. Assouline, A. Lustiger, A. H. Barber, C. A. Cooper, E. Klein, E. Wachtel and H. D. Wagner, *Journal of Polymer Science: Part B: Polymer Physics*, **41** (2003) 520.
- [31] I. Valentini, J. Biagiotti, M. A. López-Manchado, S. Santucci and J. M. Kenny, *Polymer Engineering and Science*, **44** (2004) 303.
- [32] W. Leelapornpit, M.-T. Ton-That, F. Perrin-Sarazin, C. C. Cole, J. Denault and B. Simard, *Journal of Polymer Science: Part B: Polymer Physics*, **43** (2005) 2445.
- [33] J. Li, Z. Fang, L. Tong, A. Gu and F. Liu, *Journal of Polymer Science: Part B: Polymer Physics*, **44** (2006) 1499.
- [34] T.-M. Wu and E.-C. Chen, *Journal of Polymer Science: Part B: Polymer Physics*, **44** (2006) 598.
- [35] M. Trujillo, M. L. Arnal, A. J. Müller, S. Bredieu, D. Boudieu, P. Dubois, L. W. Hamley and V. Castelletto, *Macromolecules*, **41** (2008) 2087.
- [36] M. I. Aranguren, *Polymer*, **39** (1998) 4897.
- [37] D. Fragadakis, P. Pitsis and L. Bokobza, *Polymer*, **46** (2005) 6001.
- [38] J. Xu, K. M. Razeeb and S. Roy, *Journal of Polymer Science: Part B: Polymer Physics*, **46** (2008) 1845.